

A PRACTICAL HANDBOOK

9/80 FLT

OF

DYEING AND CALICO-PRINTING.

BY

WILLIAM CROOKES, F.R.S., &c.

WITH ELEVEN PAGE PLANS, FORTY-SEVEN SPECIMENS OF DYED AND PRINTED PAGRICS, AND THIRTY-EIGHT WOODCUTS.

SPECIAL TP 930 C94 1874

LONDON:

LONGMANS, GREEN, AND CO.,

1874.

PREFACE.

Auxiliary Arts has hitherto been a desideratum in English technological literature. In repeating this very common remark we must not be understood as undervaluing the writings of Bancroft, O'Neill, Parnell, Napier, &c., nor the articles on Calico Printing contained in Dr. Ure's "Dictionary of Arts, Manufactures, and Mines," and in Muspratt's "Chemistry." But none of these works and treatises, however meritorious, can be said to cover the whole of the subject. Most of them, further, may in great measure be considered as possessing now a historical rather than a practical value, having been written prior to the wonderful development which tinctorial chemistry has experienced with the last few years. Manuals of Dyeing and Printing composed before the discovery of the coal-tar colours are now little more than literary curiosities.

To meet this want the author has undertaken the task of laying before the public in a compact, and, it is hoped, useful form, a digest of the vast mass of information on the tinctorial arts found scattered in distinct works, and in the scientific and technical journals of all nations. Much has been of necessity omitted.

To give the briefest notice of every process tried on a practical scale, much more of every laboratory experiment on the production and application of colours, would require not a volume, but a library. The author's object has been, therefore,—omitting

procedures useless from their costliness, their uncertainty, and the inferiority of their results,—to select matter which, if not positively valuable in itself, may be suggestive. It is hoped that the information here collected, from sources rare and not easily accessible, may not be without its value.

At the same time this book will not be found a mere compilation of matter which already exists in print. The author has been fortunate in obtaining the active co-operation of some of the highest practical authorities in dyeing, printing, and the manufacture of colours, and the work has been largely enriched by their suggestions and the results of their experimental researches. The kindness in this respect of Mr. S. Barlow, the late lamented Dr. F. CRACE-CALVERT, Mr. DALE, Mr. J. HIGGIN, Dr. R. ANGUS SMITH, Dr. SCHUNCK, of Manchester, and Mr. W. H. PERKIN, of London, cannot be too warmly acknowledged. The author has also the pleasure of expressing his obligations to Messrs. Brooke, Simpson, and Spiller, to Messrs. W. CRUM and Co., the late Mr. J. LIGHTFOOT, with his successors, Messrs. Grafton and Co., and Messrs. Wood and Wright, for important information furnished, and for patterns of dyed and printed fabrics supplied.

None can be more fully sensible than the author of the difficulty of doing justice to a subject so vast, so complicated, and so rapid in its growth; but he sincerely trusts that, however much his work fall short of perfection, it may still point out remunerative fields of research to the student, and assist in the development of British industry.

CONTENTS.

1	PAGE
Introduction	1
DIVISION I.	
CHAPTER I.	
THE ART OF DYEING IN ITS RELATION TO CHEMISTRY	9
Water—Tests for Impurities, 10. Lime—Magnesia—Potash—Soda —Iron—Arsenious and Arsenic Acids, 11. Organic Matter, 13. Boiler Incrustations, 14.	
CHAPTER II.	
TEXTILE FIBRES AND TISSUES MADE THEREFROM—THICKENINGS AND PLASTIC MORDANTS	16
CHAPTER III.	
COTTON	21
Mummy Cloth, 21. Cotton Wax, 34. Fatty Acid from Cotton, 36. Colouring Matter, a, 37. Colouring Matter, b, 39. Pectic Acid, 40.	
CHAPTER IV.	
Bleaching Muslins—Bleaching Cotton Stockings, 50. Bleaching Cotton Stockings Merino Shade, 51. Bleaching Cotton Stockings with Turkey-red Tops—Bleaching Raw Cotton in Small Quantities—The Continuous Process of Bleaching, 52. Bleaching with other Chemical Agents, 56.	44

CHAPTER V.

P/	AGE
Bleaching Linen—White, 57. Bleaching Linen Yarn—Colouring Linen Yarn for Carpets on the Small Scale, 58. Yellow, Green, Red, 59. Orange with Madder—Orange with Annatto—Brown and Maroon— Crimson, 60. Pensée Brown—Magenta—Aniline Purple—Aniline Blue—Prussian Blue—Lilac, 61. Bismarck Slate—Cutch Brown (Fast)—Black—Another Black, a Fast Colour, 62.	57
CHAPTER VI.	
HEMP, CHINESE GRASS, JUTE, AND OTHER FIBRES	63
CHAPTER VII.	
THE MEANS OF DISTINGUISHING VEGETABLE FIBRES FROM EACH OTHER	65
CHAPTER VIII.	
VEGETABLE THICKENINGS	66
CHAPTER IX.	
Animal Fibres—Thickenings of Animal Origin	73
CHAPTER X.	
REVIEW OF THE METHOD OF APPLYING ALBUMENOID SUBSTANCES IN THE FIXING OF COLOURS	80
CHAPTER XI.	
Wool, 82. Bleaching Wool, 82.	82
CHAPTER XII.	
PRACTICAL RECIPES IN CONNECTION WITH WOOLLEN YARN AND FABRICS Bleaching—Another Method of Bleaching, 88. Colours on Woollens— Blues—Woad, 89. Soda or Potash Vat—A Decomposed Vat—Applications of the Woad Vat—Indigo Blue on Wool for Topped Hosiery—Dark Blue for Wool for Broadcloth—Topped Logwood Blue, 90. Indigo Blue, part Logwood—Purple Blue—Chrome Blue—Dark Indigo Blue—Saxony Blue—Fast Prussian Blue, 91. Aniline Blue—Reds on Wool—Scarlet—Scarlet Lac-dye—Cochineal Scarlet, 92.	88

Ponceau-Pink for Listings-Madder Red-Magenta-Crimson with

PAGE

Cochineal - Rose Pink, 93. Dahlia - Maroon - Yellows - Belge Yellow-Orange-Salmon-Salmon with Madder, 94. Greens-Green for Broadcloth-Another Green for Broadcloth-Logwood Green-Chrome Green-Green for Yarn, 95. Aniline Green-Aniline Green with Picric Acid—Olive Green—Olives—Bichrome Olive—A Cheap Olive, 96. Olive on Zephyr-Browns-Chrome Brown-Chrome Red Brown-Camwood Brown-Fast Brown-Light Brown, 97. Bismarck Aniline Bismarck-Mode with Indigo Bottom-Mode without Indigo Drab-Slates, 98. Purple Slate-Stone Colour-Silver Grey—Lavender—Aniline Purple—Blacks—Chrome Blacks, 99. Sumach Black-Fast Black-Cheap Black-Black for Silk Striped Thibets-Colours on Wool and Warps-Slates and Modes on White Warps, 100. Magenta on Cotton Warps-Purple on Cotton Warps -Scarlet on Cotton Warps Saxon Blue on Cotton Warps Aniline Blue on Cotton Warps—Black and Orange on Cotton Warps—Green on White Warps, 101. Randoms or Clouded Yarns-Scarlet Random -- Orange Random-Saxon Blue Random, 102. Prussian Blue Random-Magenta Random-Purple Random, 103.

CHAPTER XIII.

SILK															104
Blea	ching	Silk,	106.	Means	of	Dist	ingu	ishir	ıg .	Silk	and	other	Fibr	es,	
10	7. N	I anill:	a—Si	zal—Ne	w 2	Zealar	nd F	lax-	-P	horn	nium	Tena	x, 10	7.	

CHAPTER XIV.

OTABIL, DODA, ARD DIME DALIS
Potash, 110. Nitrate of Potash—Bisulphate of Potash—Chromate of
Potash—Oxalate of Potash, 111. Manganate of Potash—Perman-
ganate of Potash-Tartar-Potash Water Glass, 112. Chlorate of
Potash-Hypochlorite of Potash-Soda Salts-Carbonate of Soda,
113. Silicate of Soda, 118. Chloride of Sodium-Hypochlorite of
Soda—Phosphate of Soda—Permanganate of Soda—Tungstate of
Soda-Hyposulphite of Soda, 119. Lime Salts-Hypochlorite of
Lime—Ammoniacal Salts—Ammonia, 120. Carbonate of Ammonia
-Sal-ammoniac-Nitrate of Ammonia, 121.

CHAPTER XV.

The Test Solutions-The Litmus Solution-Normal Sulphuric Acid
Solution, 122. Normal Oxalic Acid Solution-Normal Hydrochloric
Acid Solution-Normal Nitric Acid Solution, 124. The Estimation
of Carbonated Alkalies, 125. Estimation of Caustic Alkalies, 128.
Acidimetry, 131.

CHAPTER XVI.

CHLORINE,	CHLO	RIDE	S, AND	Снг	ORIMETRY			 			132
Estimati	on of	the	Chlori	ne in	Chlorine	Water,	140	Estin	natio	n of	
Hypoc	hlorite	S. I4	I.								

DIVISION II.

CHAPTER I.

PAGE

THE GENERAL PRINCIPLES OF THE FIXATION OF COLOURING MATTER
UPON FIBROUS TEXTURES—CLASSIFICATION OF DYE-MATERIALS 142

CHAPTER II.

- White Colouring Matters—Chalk or Carbonate of Lime—Sulphate of Lime or Gypsum, 150. Sulphate of Baryta, 151. Red Mineral Pigments, 152. Vermillion Red (specimen), 153. Yellow Mineral Pigments, 150. Chrome or Canary Yellow (specimen)—Iron Buff (specimen), 155. Green Mineral Pigments, 156. Chrome Green (specimen)—Wilner, an Arsenical, Green (specimen), 157. Blue and Violet Pigments—Ultramarine, 158. Ultramarine (specimen), 160. Cyanogen Colours, 162. Dark Blue (specimen)—Light Blue (specimen), 164. Ordinary White Tin Pulp—Blue Tin Pulp, 166. Cobalt Blues, 167.
- COLOURING MATTERS OF ORGANIC ORIGIN ARTIFICIALLY OBTAINED .. 168 Colours Derived from Uric Acid-Purpurates-Murexide, 168. Purple of the Ancients-Colours Derived from Aniline and Kindred Bodies, 171. Aniline Reds, 178. Examination of Magentas, 185. Magenta (specimen)-Ponceau (specimen), 187. Aniline-Crimson-Ponceau-PERKIN'S Violet or Mauve, 187. HOFMANN'S Violet (specimen), 194. Aniline Blues, 195. Aniline Greens-Iodine Green or Bimethyl-Iodhydrate of Trimethylic Rosaniline, 202. Nicholson's Blue (specimen) - Saffranine Pink (specimen), 203. Soluble Green, 204. Crystalline Green-Aldehyde Green, 205. Rosanaphthylamine or Naphthylamine Red-Geranosine, 206. Saffranine-Phænicine-Aniline Browns, 207. Aniline Yellows and Oranges, 209. Aniline Orange-Aniline Greys, 210. Aniline Black, 211. Aniline Black (specimen) - Coloured Derivatives of Phenol, 215. Aurine Orange-Coralline Yellow, 217. Isopurpuric Acid, 219. Rothine or Phenicienne-Vesuvine-Naphthalin Colours, 220. Naphthylamine Violets-Naphthylen Diamine Violets-Naphthalin Yellow, 221. Anthracen Colours-Artificial Alizarin, 222. Reds-Pinks-Red for Mosaics-Another Red without Oil, 225. Purple-Thickening for Purple-Thickening for Reds-Acetate of Alumina-Nitrate of Alumina, 226. Acetate of Lime-Brown, 227.

CHAPTER IV.

COLOURING MATTERS OF VEGETABLE AND ANIMAL ORIGIN 228
Madder and other Rubiaceæ, 228. Substances Soluble in Cold Water
—Glucose—Cane Sugar—Gum and Mucilage, 233. Pectose—
Chlorogenin—Alkaline Tartrates—Malates—Citrates—Substances
Soluble in Boiling Water and in Alcohol, 234. Rubian, 239. Alizarin,
245. Purpurin, 247. Original Colours Soluble in Water—Glucosides

-Rubian--Rubervthric Acid - Colouring Matters the Existence of which cannot be Doubted -- Alizarin -- Purpurin -- Orange Matter-Pseudopurpusin - Purpuroxanthin - Xanthopurpurin - Colouring Matters of Doubtful Existence or which Require Further Investigation-Yellow Matters-Resinous Matters-Commercial Products or Derivatives from Madder, 252. Garanceux, 261. Mechanical Process of Purifying Madder, 263. Testing of Madders-Fleur de Garance-Garancin Extracts, 269. Use and Application made of Madder and its Preparation for Dyeing Purposes, 273. Bleaching-Printing and Fixing the Mordants-Mordants for Red-Pink-Rose Colour, 275. Strong Mordant No. 1-Mordant No. 2-Strong Mordant, 283. 5 4 Mordant-Red Mordant (Liquor) for Garancin-Strong Mordant-Mordant for Red with Garancin, 284. Red Mordant for Madder-Bright Red-Red Mordant-For Deep Red-Red Liquor or Mordant-Other Red Mordant-Red 4/2-Mordants for Rose Colour -Pink, 288. Red Liquors from Acetate of Lime-Red Liquor for Madder Pink (Rose Colour), 289. Mordants for Brown and Chocolates, 292. A. Ordinary Madder Style Work, 307. B. Garancin Style, 308. Madder-Printing, 315. Discharge and Resist Processes, 317. Reserves, 319. Turkey-red, 321. Madder (specimen)-Artificial Alizarin (specimen), 326. Substitutes for Madder, 329.

CHAPTER IV.*

Santal Wood-Sanders Wood or Red Sanders, 339. Caliatur or Cariatur Wood-Madagascar Wood-Barwood, 341. Camwood or Kambe Wood-Logwood or Campeachy, 342. Red Colouring Matters -Cochineal-Kermes-Lac-lake-Gum-lac-Lac-dye, 350. Animal or Vegetable Kermes-Scarlet Grain-Oak Cochineal-Gum-lac or Resin-lac, 353. Shellac, 354. Carminic Acid, 357. Ammoniacal Cochineal, 358. Carmine, 359. Harmala Red—Erythrose, 364. Fustic Carmine-Preparation of Lake Colours-A. Red Lakes-Madder Lake, 365. Lakes of the Red Woods-Cochineal Lakes-B. Blue Lakes-C. Green Lakes, 366. D. Yellow and Orange Lakes-Annatto Lakes -Fustic Lakes-Aniline Lakes-Colouring Matters Derived from Lichens, 367. Chemical History of the Colouring Matters of Lichens, 369. Erythric Acid-Erythrine, 370. Picrocrythine, 371. Orsellic or a-Orsellinic Acid—Lecanoric, Diorsellic, a-Orsellic Acid, or Lecanorine, 372. Rocellinine-Parelline, or Parellic Acid-Colouring Matters of Orchil, 374. New Methods of Preparing Orchil, 375. Applications of Orchil in Dyeing and Printing, 379. Amaranth Red-Amaranth Bright-Amaranth Violet-Feuille Morte -Novel Colour, 380. Litmus, 381. Alkanet-Safflower, 384. Carthamin, 385.

CHAPTER V.

Sooranjee-Root of the Morinda citrifolia, 391. Ænolin, or Red Colouring Matters of Wine, 392. Yellow Vegetable Colours, 393. Quercitron, 395. Colouring Matters contained in Quercetin, 396. Use made of Quercitron, 401. Persian Berries, 403. Fustic-Yellow Brazil Wood-Cuba Wood-Yellow Wood-Old Fustic, 405. Morintannic Acid, 406. Weld, 408. Rutin-Robinin, 410. Rhamnoxanthin-Colouring Matter of Thuya occidentalis-Fustet-Young Fustic-Zante Fustic, 411. Colouring Matter from Buckwheat, 412. Dyeing with Weld, 413. Upon Cotton, 414. Aloes, 415. Turmeric, 418. Yellow Colouring Matters of Chinese Origin, 421. Saffron, 422. Barberry Bark, 423. Yellow Colouring Matters contained in Flowers-Carotin-Yellow Colouring Matter of Carrot-Roots, 424. Purrhee or Indian Yellow-Yellow Colouring Matters of the Lichens-Chrysophanic, Vulpic, and Usnic Acids, 425. Chrysinic Acid-Gentianic Acid-Annatto or Anotto, also known as Rocou, Bixin, or Orleans, 426. Green Colouring Matters-Chinese Green-Lokao, 428. Green Dyeing, 432. French Process for Dyeing with Lokao, 433. Other Green Dyes of Vegetable Origin, 434. Chlorophyl-Chromule-Green Colouring Matter of Leaves and other Green Parts of Plants, 435. Blue Colouring Substances, 438. Indigotin, 439. Sulphindigotic Acid, 445. Indigo, 447. Woad or Pastel, 453. Industrially-prepared Sulphuric Acid Derivatives of Indigo-Lindigo-Carmine - Purple-Blue, also known as Boiley Blue, 463. Fixing Indigotin by the Reduction Method, 468. Reduction of Indigo-Theory of Indigo-Vats, 469

CHAPTER VI.

Brown and Black Colouring Matters—Astringents 490 Kino, 491. Catechu, 493. True Astringents-Galls, 499. Gallein -Alder Bark, 508. Algaroba-Amalic Acid-Anthokirrin-Areca Nuts-Bablah-Neb-neb-Neb-nab-Babulah-Barbatimas-Bearberry-Bilberries, 509. Brauna Wood-Butter-nut Bark-Cactin-Canadian Yellow-root—Carapa-root—Chestnut—Chicory—Chrysoretin - Coccedia viridis - Cocoa-nut Tree - Cork, 510. Dyer's Woodruf - Gammam - Golden-rod - Green Ebony - Heath - Hellebore -Hemlock - Hiccory-Holly-Hollyhock - Horse-chestnut - Horseradish - Khailcedra - Lamium album - Lamium purpureum - Lawsonia inermis-Lithospermum arvense, 511. Mahaleb-Mahogany Tree Bark - Mangrove - Nitrocuminic Acid - Nucin - Nymphæa alba - Palisander Wood - Paracarthamin - Phycocyan - Pittacal -Polygonum tinctorium - Pomegranate-root Bark - Purple Heart-Privet Berries, 512. Saw-wort—Sunflower Seeds—Syria—Viridic Acid-Virginia Creeper-Preparation of Extracts of Dye-Woods, 513.

CHAPTER VII.

Mordants, technically known as "Tin-Spirits," 519. Proto-Salts of
Tin and their Solutions, 522. Double Muriate of Tin, 523. Single
Muriate of Tin—Proto-Salts of Tin-Spirits, 524. Oxalate of Tin,

PAGE

525. Claret Spirit-Sesquisalts of Tin, 526. Nitrate of Tin, 527. Purple Spirit for Wool and Worsted-Aniline Spirit-Hellor's Mordant, 528. Stannic Salts, or Per-salts of Tin, 529. Bichloride, Perchloride, or Tetrachloride of Tin-Stannic Chloride-Chlorostannic Acid-Fuming Spirit of Libavius-Aqueous Bichloride, or Stannic Chloride of Tin-Red Cotton Spirits, known as Crimson Spirits, 530. Barwood Spirit-Plum Spirit-Solution of Tin, 531. No. 2 Solution-Oxymuriate of Tin-Pink Salt, 532. Alumina Mordants-Aluminate of Soda-Aluminate of Potash, 534. Iron Mordants-Copperas-Green Vitriol-Protosulphate of Iron-Ferrous Sulphate, 535. Persulphate of Iron-Muriate of Iron-Permuriate of Iron-Black Liquor-Nitrate of Iron, 536. Common Iron for Drabs, 539. Alkaline Iron Mordants-Lead Mordants-Nitrate of Lead-Sulphate of Lead-Alkaline Solutions of Lead, 541. Tungsten Mordants-Antimony Mordants, 542. Bismuth Mordants, 543. Chromium Mordants, 544. Manganese Mordants-Zinc Mordants-Arsenic Mordants-Copper Mordants, 545. Ammoniuret of Copper, 546. Chloride or Muriate of Copper-Nitrate of Copper-Sulphate of Copper, 547. Tartar and Argols, 548. Tartaric Acid, 549. Super Argol-Royal Blue Spirits, 550

CHAPTER VIII.

Perrotine, 551. Cy inder Machines, 560. Mixing Colour, 561. Thickeners, 563. Madder Colours, with Several Variations-Garancin Colours-Reserved Style, 564. Padding Styles-Indigo Blues-China Blues-Turkey Red, with Discharges-Steam-Colours -Spirit-Colours, 565. Bronzes-Pigment-Colours-First Style-Madder, 566. Mordants - Discharges - Reserves - Covers, 572. Plate Style-Plate Pinks, 575. Madder Red and Pink (specimen), 576. Madder Style, First Stage (specimen)-Madder Style, after Dyeing (specimen), 577. Madder Style, after Clearing (specimen), 578. Madder and Aniline Black (specimen)—Garancin (specimen)—Third Style, Reserved, 580. Fourth Style-Padding, 581. Fifth Style-Indigo Effects, 585. Indigo Style, First Stage (specimen), 590. Indigo Style, Second Stage (specimen)—Indigo Style, with other Colours, Third Stage, 591. Style produced by Lightfoot's Patent Process (specimen), 592. Sixth Style-China (Indigo) Blues, 593. Seventh Style -Discharges on Turkey Reds, 594. Eighth Style-Steam-Colours, 598. Standard Brown, Light (specimen)-Standard Brown, Dark (specimen), 604. Aloes Green, 607. Cochineal Pink (specimen), 609. Pale Yellow, from Persian Berries (specimen)-Dark Yellow, from Persian Berries (specimen), 612. Hofmann Violet on Calico (specimen) -Delaines, 613. Printing Delaines, 617. Woollen Goods, 624. Silks, 630. Ninth Style-Spirit-Colours-Application Colours, 635. Tenth Style-Manganese Bronzes, 638. Eleventh Style-Pigment Printing, 639. Guignet's Green and Chrome-Green-Chrome-Black and Dichromate of Lead (specimen)—Ultramarine Blue, Chrome-Black, and Dichromate of Lead, 641. Ultramarine and Madder Extract (specimen) - Carbonaceous Grey, with Chrome-Black - Chrome-Green, Chrome-Yellow, and Extract of Madder (specimen), 643. Extract of Madder, Red and Pink, with Chrome-Orange, Green, Ultramarine Blue, and Chrome-Black (specimen). 644. Green Padded Ground, with Design in Madder, Red, and Pink, Chrome-Orange, Green, and Black (specimen)—Chrome-Orange, Light and Dark (specimen), 645. Aniline Black, with Madder Red and Chrome-Orange (specimen), 647. Aniline Black, 649. Murexide Purples, 650. Operations Accessory to Dyeing, 651. Influence of Light upon Colours, 655. Action of Light, 659.

CHAPTER IX.

APPENDIX.

Preparation of Picric Acid, 673. Isopurpuric Acid—Rosolic Acid— FoL's Yellow-Campo-Bello Yellow-Phenicienne-Chloride of Benzyl, 674. Diphenylamine—Cerise—Coupier's Aniline Reds—Hof-MANN'S Xylidin Red, 675. ULRICH'S Scarlet - Hofmann Violet, R.R.R.—Dorothea Violet—WANKLYN'S Violet—Paris Violet (Poir-RIER'S Violet), 676. Hofmann Violet, R.R.R. (specimen)—SPILLER'S Purple (specimen)—Lauth's Violet, 677. Methyl-diphenylamine Violet-Paris Green-Methylaniline Green-French Yellow; Chryseic Acid (Nitro-xynaphthalic Acid of Dusart and Gelis), 678. Carminaphtha—Chloroxy-naphthalic Acid—Ballo's Violet—Naphthoic Blue, 679. Aniline Grey, CASTELHAZ (specimen)-Naphthols, or Naphthylic Alcohols, 680. Anthracen-Orange, 681. Artificial Isopurpurin, 682. Anthrapurpurin—Aurin (Yellow Corallin, Rosolic Acid), 683. Derivatives of Resorcin—Derivatives of Hydroquinon—Derivatives of Pyrocatechin—Gallein, 684. Nitrous Derivatives of Resorcin-Cyanin, 685. Aloes-Dalleiochin, 686. Rufigallic Acid, 687. Adulteration of Albumen-Dyeing Aniline Blacks on Cotton Yarn-Printing-Ink for Use in Calico-Printing, 688. New Iron Mordant-New Aniline Red-Printing Aniline Colours on Calico-Use of Epsom Salts in Dyeing-Test for Saffranin-Cochineal-Red on Cotton, 689 .- Method of Determining Anthracen-New Class of Colouring Matters, 690 Vat-Blue Ground, with a Red, Brown, Black, and White Pattern, 691. Black and White on a Madder Red Ground -Dark Spirit Violet on Cotton Warps, 692. DALE'S Patent Process for Printing and Dyeing with Aniline Colours, 693. Artificial Orchil, 604. Chemical Removal of "Burls" from Wool and Woollen Goods, 695. Coralline—Hydrometer Tables—BAUME's Scale—BECK's Scale-Cartier's Scale, 697. Thermometer Scales, 699. Decimal or Metric Weights and Measures-Measures of Length, 699. Superficial Measures-Measures of Capacity, 700. Weights, 701. Bibliography, 702.

LIST OF PAGE PLATES.

Dye House at the Gobelins, Paris	. 1	(Frontist	iece.)
Plan of Dye Works	To f	ace page	88
Manufacture of Aniline Blue	11	3 7	176
Retorts for Distilling Methyl-Aniline	2.1	2.2	192
Block-Printing. Painting in Reserves by Hand	2.2	11	292
Gas-Process for Engraving Blocks for Printing. Designs			
Produced by the Gas-Process ,	,,	11	551
Blocks Successively Applied to Produce the Different	t		
Shades in a Design. Machine for Engraving Copper			
Cylinders	,,	7.7	. 554
Singeing House	11	11	608
Washing-Machine for Blacks			624
Drying Apparatus	12		640
Finishing-Machine	,,		.6-6

LIST OF WOOD ENGRAVINGS.

	PAGE
Barlow's Method of Bleaching under Pressure	46, 47
Bentley's Continuous Process of Bleaching	53, 54
Elevation and Ground Plan of a Bleach House	55, 56
Fibres of Cotton, Silk, and Woollen Fibres	108, 109
Lixiviation Process	115
Alkalimeter Tube	123
Preparation of Aniline Red	180, 182
Preparation of Aniline Violet	193
Preparation of Aniline Blue	198
Preparation of Aniline Green	203
Preparation of Alizarin	268
Madder Dyeing	306
Preparation of Dye-woods	514
Perrotine Machine for Printing	552, 553
Cylinder Machine for Printing	555
End Elevation and Section of a 4-Colour Machine	556, 557
12-Colour Machine	559
20-Colour Machine	559
8-Colour Machine	560
Colour Mixing Pans	561
Graining Machine	562
Padding Flue	582
Apparatus for Sulphuring Delaines	164

SPECIMENS OF DYED AND PRINTED FABRICS.

	PAGE
Vermillion-Red	153
Chrome-Yellow (Canary)	155
Iron Buff	155
Chrome-Green	157 -
Wilner Green (Arsenical)	157
Chrome-Yellow (Canary) Iron Buff Chrome-Green Wilner Green (Arsenical) Ultramarine Dark Prussian Blue Light do. do.	160
Dark Prussian Blue	164
Light do. do	164
Magenta Ponceau (Brooke, Simpson, and Spiller's)	186
Ponceau (Brooke, Simpson, and Spiller's)	186
Hofmann's Violet, B	194
Hofmann's Violet, B	203
Saffranine Pink	203
Aniline Black	215
Aurine Orange	217
Coralline Yellow	217
Turkey Red, Madder	326
Do. Artificial Alizarin	326
Madder, Red and Pink	576
Madder Style, First Stage	577
Do. after Dyeing	577
Do. after Clearing	578
Madder with Aniline Black	579
Saffranine Pink Aniline Black Aurine Orange Coralline Yellow Turkey Red, Madder Do. Artificial Alizarin Madder, Red and Pink Madder Style, First Stage Do. after Dyeing Do. after Clearing Madder with Aniline Black Garancin Indigo (Lightfoot's), First Stage	579
Garancin	590
Do. do. Second do	591
Do. do. Third do	591
Style produced by Lightfoot's Patent	592
Do. do	592
Brown (Catechu), Light	. 604
Do. do. Dark	604
Style produced by Lightfoot's Patent Do. do. Brown (Catechu), Light Do. do. Dark Cochineal Pink Yellow, Pale (Persian Berries) Do. Dark do. Hofmann Violet (Calico) Guignet's Green and Chrome-Green, Chrome-Black, and Dichromate o	. 609
Yellow, Pale (Persian Berries)	612
Do. Dark do	. 612
Hofmann Violet (Calico)	613
Lead	. 641
Ultramarine Blue, Chrome-Black, and Dichromate of Lead	641
Ultramarine with Vermillion and Chrome	. 642
Ultramarine with Vermillion and Chrome Do. with Madder Extract Carbonaceous Grey, with Chrome-Black, Chrome-Green, Chrome-Yellov	643
Carbonaceous Grey, with Chrome-Black, Chrome-Green, Chrome-Yellov	,V,
and Extract of Madder	. 643
Extract of Madder, Red and Pink, with Chrome-Orange, Green, Ultra	- 6
marine Blue, and Chrome-Black	644
Green Padded Ground, with Design in Madder, Red and Pink, Chrome	- 6
Orange, Green, and Black Chrome-Orange, Light and Dark	. 645
Onrome-Orange, Light and Dark	645
Aniline Black, with Madder Red and Chrome-Orange	. 647
Hofmann Violet, R.R.R	677
Apiline Cross (Contollog)	. 677 680
Aniline Grey (Castelhaz)	000

A HANDBOOK

OF

DYEING AND CALICO PRINTING.

INTRODUCTION.

THE introduction of a number of new dyes resulting from chemical research has rendered very desirable the publication of a complete work containing the latest and most reliable information on the subject, and nevertheless confined within reasonable limits.

Few branches of human industry are more intimately connected with science than the art of dyeing and printing, that is to say, the application of colouring matter to vegetable and animal tissue. To recount the numerous branches of science with which the art of dyeing is more or less associated would be tedious and unprofitable, but the following instance will serve as an example: -The substance known as cochineal, which in its native country, Mexico, was used as a dye and cultivated by artificial means at a very remote period of history, was long supposed to be the dried seed of a plant. After the year 1518 it was introduced into Europe, but its real constitution was not known until the 17th century, when it was accidentally discovered to consist of the body of an insect, the Coccus cacti. The dye yielded by cochineal being valuable, and capable of producing many shades of colour, attempts were soon made to introduce into other countries the plant upon which the insect lives and feeds. To do this with success it became necessary to study minutely the habits of a very small insea, and to inquire attentively into the climatological and all other conditions of its life. Nor was this all, for recent experience has taught us that even in localities favourable to the growth of the species of cactus upon which the insect lives, the Coccus cacti itself languishes or becomes extinct if the spot where it is located be too near the sea and subject to the influence of damp winds. Here is a demonstration of simultaneous connection with the sciences of Natural History, Botany, and even Meteorology. The position of the art of dyeing and printing with

regard to Chemistry and Mechanical Science is too obvious for comment, but attention must be drawn to the important fact that, notwithstanding the progress made in those sciences with which the art has more or less in common, our knowledge of the subject itself is but slight. We are entirely ignorant of the laws which govern the combination of dyes and pigments with fibrous tissue, and totally unable to point out the chemical difference between white and coloured fibre, or to explain the causes of the appearance or disappearance of colour. There is not a single experiment on record which will enable the reader to judge whether colouring tissue by dyeing is a chemical phenomenon or not; neither does there exist a quantitative determination of the amount of alumina, iron, or tin, which may combine with or be attached to cotton, wool, or silk. It is, moreover, still uncertain how much colouring matter may combine with these metals, and whether any definite compounds exist; in fact, there is no chemical theory of dyeing worthy of the name.

The history of dyeing is another question.

Its invention or discovery may be said to have been coeval with the first traces of civilisation; it is impossible to determine the time when the art of imparting colours to fabrics was first practised, but there is reliable historical evidence as to its antiquity. In those portions of Asia where at a remote period there existed a high degree of civilisation, a somewhat advanced proficiency in the art appears to have been reached, especially in Phœnicia, whose capital city, Tyre, was the Manchester of antiquity, and about fourteen or fifteen centuries before the Christian era became celebrated for the production and application of the famous Tyrian purple.

According to Pliny and Aristotle, this valuable and costly dye was obtained from a kind of mollusc, a little reservoir in the throat of which on being pierced yielded one single drop of liquid. This liquid, at first colourless, became gradually lemon-coloured, then sky blue, and in a few days purple.

Bancroft ("On Permanent Colours") says regarding it:-

"To avoid the trouble of opening the small reservoir in each fish the smallest species was generally bruised whole in a mortar, though the other fluids of the fish must have necessarily debased the colour in some degree. The liquor when extracted was mixed with a considerable portion of salt to preserve it from putrefaction, and was then diluted with five or six times as much water, and kept moderately hot in leaden or tin vessels for the space of ten days, during which the liquor was often skimmed to separate all impurities; after which the wool, being first well washed, was immersed and kept therein for five hours, then taken out, carded, and again immersed, and continued in the liquor until all the colour was exhausted. To produce particular shades of colour, nitre, urine, and a marine plant called Fucus were Several of these varieties of colour have been paroccasionally added. ticularly mentioned by ancient writers. One of them, which was very dark, seems to have been a violet, inclining towards the reddish hue; 'Nigrantis rosæ colore sublucens' (Pliny, lib. ix., sect. 50). Another, and less esteemed, was probably a kind of crimson; but the most esteemed, and that in which the Tyrians particularly excelled, resembled coagulated blood; 'laus ei summa in colore sanguinis concreti' (Pliny, sect. 62). There was, moreover, a fourth kind known in later times, an account of which may be found in

Perrault's translation of 'Vitruvius.' Pliny says 'the Tyrians first dyed their wool in the liquor of the purpura, and afterwards in that of the buccinum; the purple mentioned in Exodus, chap. xxv., was also twice dyed. Wool which had received this double Tyrian dye (dibapha) was so very costly, that in the reign of Augustus each pound of it sold for 1000 Roman denarii (about £36 sterling). But lest this should not sufficiently exclude the use of it from all who were not invested with the highest dignities, laws were made inflicting severe penalties, and even that of death under the later emperors, upon all who might presume to wear it. The art of dyeing this colour came at length to be practised only by a few individuals, appointed and maintained by the emperors for that purpose; and it being interrupted about the beginning of the 12th century all knowledge of it was soon after lost, except what remained in the more ancient writings; and during several ages this celebrated dye was considered and lamented as an irrecoverable loss."

This dye, in addition to its beauty, must also have been very fast, for it is recorded that when the town of Susawas taken by the Greeks a large and valuable collection of purple cloth was found amongst the treasures of the Persian king Darius, and notwithstanding it had been kept for a period of 190 years, its lustre and beauty were undiminished. This account may be received as substantially correct, inasmuch as it is related by no less a person than Plutarch. A complete history of this subject would occupy the entire space of a large volume, but the following brief outline may prove useful to the reader.

"The earliest important event in the history of dyeing was the discovery of the effects of bases or mordants, and particularly that of alum in fixing adjective colouring matters. When or where this discovery was first made cannot be ascertained; there is, however, good reason to believe that alum and probably iron salts (which are the principal bases of modern calico printing) were employed by the Egyptians in producing those effects which are described by Pliny, lib. xxxv., sect. 42; because they resemble others which calico printers now obtain by these means, and which at this time they cannot obtain by any other, even with all the knowledge since acquired; and it has been proved that the Egyptians borrowed this art from Hindostan, where it appears to have subsisted for more than 2000 years, probably with very little if any variation or improvement during that long space of time; and if we may judge of the means formerly employed in Hindostan for dyeing or staining calicos by those which were found to be in use for that purpose when the nations of Europe first went thither by the Cape of Good Hope, we may safely conclude that solutions of alum and of iron must have been the mordants employed in fixing the adjective colours."-BANCROFT, "On Permanent Colours."

Very little is now known as to the proficiency of the ancient inhabitants of India in the arts of dyeing and weaving, but there is evidence to prove that the ancient nations who dwelt in that portion of Asia just alluded to, and also the ancient inhabitants of Mexico and Peru, enjoyed an advanced degree of civilisation, and were by no means wanting in skill in applying colours to woven tissues. Notwithstanding the æsthetical progress in civilisation made by the Greeks, they appear to have advanced but little in the art of colouring woven fabrics, and were in this respect greatly behind the ancient Romans.

No records remain regarding the operations carried out and processes invented by the latter, but it is certain that they were acquainted with the use of such substances as madder, woad, nutgalls, and alkanet root, and with the application of blue and green vitriol, alum, and even some salts of lead. According to Dioscorides and Pliny, who lived in the 1st century, indigo was known in Europe, and although scarce, was regularly imported from India, whence its name is derived. The natives precipitated and collected in a dry solid form the colouring matter of indigo, and, what must have been a much greater difficulty, they afterwards discovered the means of dissolving it and rendering it capable of being permanently fixed upon the substances intended to be stained or dyed with it; an effect which the Greeks and Romans do not appear to have ever produced, though they knew how to powder and apply indigo as a paint.

"It appears that wool* was never worn in China but as a substitute for fur, and that cotton and silk, being the only substances ever dyed by the inhabitants, received all their colours from vegetable tinctorial matters; that these colours were principally red, blue, violet, and what is called a woad colour; and that under the three first dynasties the business of dyeing was chiefly practised by the female part of each family for its own particular use: and it probably continued to be practised without anything like principle or science until near the end of the 7th century, when the Chinese, discarding their own, borrowed the art and means of dyeing which were then in use among the Hindoos and Persians; and it is said that alum and copperas, which the Chinese did not use before, were among the means so borrowed, a fact which renders it probable that there was little, if anything, in the Chinese art of dyeing of which the loss need now be regretted.

"It appears, however, that long before this time a knowledge of the uses of alum and of iron salts in dyeing had spread from Hindostan and Persia westward to Egypt, and thence to Greece and Rome. Bergmann, indeed ("De Confect. Alum"), and, after him, Beckmann (in the "Göttingen Memoirs"), have represented the alum of the ancients as differing from the crystallised salt so-called by the moderns, and have supposed that the varieties of alum mentioned by Dioscorides were stalactites containing but little alum and consisting chiefly of calcareous earth, which, in certain proportions, will hereafter appear to be a very useful addition for most of the colours depending on an aluminous basis. Nature, however, does produce some, though but little, crystallised alum, particularly in Egypt and some parts of Asia, and it probably was in this state that its good effects in dyeing had been first observed, before mankind were led to the means and operations since employed for separating and collecting it from the various aluminous ores. Bergmann says that 'the factitious salt which is now called alum was first discovered in the eastern countries;' and that 'among the most early works established for the preparation of alum we may justly number that of Roccho, a city in Syria, now called Edessa: hence the appellation of roche alum (see vol. i., p. 339, of the English translation of his Essays).' He adds that 'Bartholomew Perdix, or Pernix, a merchant of Genoa, who had been at Roccho, discovered the matrix of alum in the island of Ischia, about the year 1459, and established a manufactory there; at the same time, John de Castro, who had visited the

^{*} Memoires Concernants l'Histoire, les Sciences, les Arts, les Mœurs, &c., des Chinois.

manufactories at Constantinople, discovered a matrix at Tolfa, by means of the *Ilex aquifolium*, which he had also observed to grow in the adjacent mountains of Turkey, and his opinion was confirmed by the taste of the stones. The attempts made by the Genoese at Viterbium and at Volaterre succeeded extremely well; the preparation of alum in Italy soon increased wonderfully fast, &c. The first manufactory in England was established in the reign of Elizabeth, at Gisborough, by one Thomas Chaloner."—BANCROFT, "On Permanent Colours."

When Italy was overrun by those barbarous nations who came from the north-east of Europe, the progress of all arts and sciences and of all human industry belonging to advanced civilisation was stopped, and remained so during at least five centuries, except in a small portion of Spain. Here the so-called Saracens succeeded in establishing a settled state of society, and, as evidenced by the records they left, attained high proficiency in manufacturing arts, such as paper making, sugar refining, and the extraction of dyes from native vegetable produce. They were, doubtless, acquainted with the process of dyeing the so-called Turkey red, as the means of producing that dye on tissues were known at the time at Adrianopolis, in Turkey.

In the Middle Ages, the Jews were perhaps the greatest dyers. During what is often called the Revival Period of Literature and Science, to wit, the end of the 12th and beginning of the 13th centuries, the Republic of Florence became not only the seat of civilisation, but of a thorough revival of industry and

manufacture, especially as regards dyeing.

"According to M. Berthollet, whatever knowledge the Greeks and Romans had derived from others or acquired from their own observations appears to have been in a great degree lost about the 5th century, when scarce any traces of science, industry, or humanity were left in what was then called the Western Empire; a little, however, did remain, and it was afterwards preserved in Italy, where the Venetians contrived to import many oriental productions and manufactures, which, by affording new means, as well as new objects of imitation,

contributed greatly to revive the arts.

"The first collection of processes used in dyeing was published at Venice in 1429 under the name of "Mariegola del'Arte dé Tintori," of which another edition, much improved, appeared in 1510; and from this an individual named Giovanne Ventura Rosetti, who travelled into different parts of Italy and the neighbouring countries, to learn the methods and means employed in dyeing, composed, and in 1548 published, a work under the title of "Plictho del'Arte de i Tintori, &c.," which has been supposed to have contributed more than any other to the improvements afterwards made in that art. In this work, however, there is no mention of either indigo or cochineal, which M. Berthollet therefore concludes were not at that time employed by the Italian dyers. This appears to have been the work which, at a meeting of the Royal Society on the 30th of April, 1662, Mr. Haak was desired to translate into the English language (see Dr. Birch's "History"). That learned body had, upon its first institution, bestowed some attention to the subject of dyeing; and on the same day Sir William Petty, one of its earliest and most active members, in consequence of a previous request from the Society, brought in "An Appendix to the History of the Common Practices of Dyeing," which was afterwards printed in Dr. Spratt's "History of the Royal Society," and seems to have been the first

account published in the English language of the means and operations used by dyers. Nearly two years afterwards, viz., March 30th, 1664, Mr. Boyle presented to the Royal Society his "Experiments and Considerations touching Colours:" and on the 10th of August following it was ordered by the Society that the way of fixing colours should be recommended to Mr. Howard, Mr. Boyle, and Dr. Merrit.' These, and especially the first two, were among the most distinguished members of the Society; but it does not appear that they were able to do anything deserving of notice, in consequence of this recommendation. However, at a meeting of the Society on the 11th November. 1660, that very ingenious and useful member, 'Mr. Hooke, produced a piece of calico stained after the way contrived by himself, which he was desired to prosecute in other colours besides those that appeared in this piece (Birch's "History of the Royal Society," vol. ii., p. 401); and, accordingly, on the oth of the following month, 'Mr. Hooke produced another specimen of staining with yellow, red, green, blue, and purple colours, which he said would endure washing with warm water and soap.' But from this time it does not appear that anything considerable was done for nearly the space of a century, by men of science in this kingdom, towards improving the arts of dveing and calico printing, they being probably discouraged by the difficulties which, from the very imperfect state of chemical science, must have occurred in every attempt to improve upon what the dyers were able to perform without any principle or theory. In France, however, the minister Colbert, anxious to extend the commerce and manufactures of that country, turned his attention particularly to the art of dyeing, with a view to amend, as well as to obviate, frauds in the practice; and for these purposes an "Instruction Générale pour la Teinture des Laines et Manufactures de Laine de toutes Nuances, et pour la Culture des Drogues ou Ingrédients qu'on Emploie" was prepared under his immediate direction, and published in 1672. This, however, was not intended merely to inform, but as a legislative act to control the dyers in their operations. It divided them into two classes; the one, dyers "en grand," were confined to the colours deemed lasting, while the dyers "en petit teint" were allowed only to give those which were considered as fugitive; and the drugs to be employed in each branch were also particularly specified, and the dyers in each prohibited from using or having in their possession any of the drugs allotted to the other. Restraints of this kind, though intended to prevent frauds, must have operated as checks upon future improvements if the government had not encouraged useful discoveries in this art, first by offering rewards, and afterwards by appointing those eminent chemists, Dusay, Hellot, Macquer, and Berthollet, in succession, to superintend and improve the arts connected with chemistry, and more especially that of dyeing.

"Dusay appears to have been the first who entertained just conceptions of one of the causes of the adhesion of colouring matters to stuffs when dyed; viz., that which depends on an affinity or attraction subsisting between such matters and the fibres or substances of the dyed stuffs. He also noticed the difference in the degree of attraction which different substances, as wool and cotton, exert upon the same colouring matters, and which he found so great that a skein of each having been in an equal degree subjected to the means and operations commonly employed for dyeing scarlet, the woollen yarn was found to be fully and permanently dyed of that colour, while the cotton

retained all its former whiteness. He appears, however, to have had no conception of the other and more important cause of the permanency of adjective colours-viz., that which arises from the interposition of a suitable basis possessing a particular attraction both for the colouring matter and for the dyed substance, and thereby acting as a bond of union between them; nor did his successor, Hellot, ever approach nearer to the truth on this subject. He (Hellot) fancied that he could discover in every dyeing process some means by which sulphate of potash might be formed; and this neutral salt not being readily soluble in cold water, nor affected by air or light, he conceived the art of dveing to consist in first dilating the pores of the substance to be dyed, so as to procure a copious admission of colouring matter, divided by a suitable preparation into atoms, and then wedging or fastening these atoms within the pores of the dyed substance by the small particles or crystals of this difficultly soluble neutral salt. Upon this mechanical hypothesis he supposed that alum became useful in dyeing, not by the pure clay or alumina which it contains, and which alone contributes to fix any colouring matter, but only by furnishing sulphuric or vitriolic acid to assist in forming the sulphate of potash, which was to perform this important function of wedging or fastening the colouring atoms; though, if he had brought this visionary hypothesis to the test of experiment, as might have been easily done, he would have found, not only that no sulphate of potash existed in many cases where he supposed it to produce such important effects, but also that, even if intentionally formed and employed for this purpose, it possessed no power whatever of fixing any colouring matter yet known. But, though nothing could be more groundless than the theory, the learned in all countries appear to have been satisfied with it for a considerable length of time, it being always less troublesome to believe than to make experiments.

"According to Mr. Henry of Manchester, M. Keir, the ingenious translator of Macquer's "Chymical Dictionary," appears to have been the first who suspected that (in dyeing) the earth of alum was precipitated, and in this form attached to the material prepared or dyed.' Some time after this, Mr. Henry published an interesting paper in the third volume of the "Memoirs of the Manchester Society," "On the Nature of Wool, Silk, and Cotton as Objects of the Art of Dyeing, on the Various Preparations and Mordants requisite for these Different Substances, and on the Nature and Properties of Colouring Matter, &c.," a paper replete with useful information and ingenious ideas."—Bancroft, "On Permanent Colours."

Trustworthy authorities state that no less than two hundred dye-works existed at Florence about the end of the r4th century. The application of colours derived from lichens, and more especially the species known as "Rocella," was so extensively and successfully carried out that, in order to prevent the process being divulged, a guild was formed which obtained the name of "Rocellarii."

The discovery of America opens a new era in the progress of dyeing. Many new dye-stuffs were then brought from that country into Europe, among which logwood, cochineal, annatto, and brazil-wood may be mentioned.

The use of tin salts as mordants was discovered about the middle of the 17th century by the Dutch chemist, Cornelius Drebbel, who found that they yielded a magnificent colour with cochineal. Drebbel's son-in-law, who

obtained from him considerable information upon the subject of dyeing, set up large dye-works at Bow, near London, in 1643, and successfully carried on an extensive business for a number of years.

The journeys to India made by the Portuguese and the inhabitants of the Netherlands early in the 17th century had the effect of again introducing indigo to the notice of European nations as a substitute for woad as a blue dve material. The farmers who cultivated the latter plant felt their interests injured by the introduction of indigo, and accordingly several governments. including our own, in the time of Elizabeth, prohibited its use, and large quantities were destroyed. A similar measure was enacted against logwood. In consequence of this prohibition, woad was still used instead of indigo long after the re-importation of the latter; and even as late as the end of the last century the dyers' foremen of Nüremburg were compelled to take an oath before the Syndic of that town to abstain from the use of indigo and employ woad only, as being the orthodox and genuine colour. However, notwithstanding the oath, when Nüremburg was taken and pillaged by the French, about 1798, large quantities of indigo were found in the town. The progress made during the 18th century in dyeing, as well as in printing calico, is too varied and extensive to be specifically alluded to here; suffice it to say that in France especially it was very great. It is more particularly from France that most other nations of Western Europe originally obtained those preparations of large establishments and manufactories which have now become so numerous, especially in Great Britain. Political commotions, for instance the repeal of the Edict of Nantes, drove a number of industrious and skilful people from France at an earlier period; they took refuge in England, the Netherlands, and Switzerland, and carried with them the knowledge of industrial art already practised in their native country. The great discoveries made in chemistry during the latter part of the last century have greatly improved and extended the application of dyes to woven fabrics, whilst the employment of steam as a motive power presents increased facilities for practising the art.

CHAPTER I.

THE ART OF DYEING IN ITS RELATION TO CHEMISTRY.

M OST operations in dyeing (the word being used here in a wider sense as applying also to the allied arts of bleaching and printing) may be considered as directly chemical, and the mechanical appliances as so much apparatus intended to facilitate or regulate the chemical action taking place between the fibre, the mordant, and the colouring matter. As this action varies in kind or degree for every colour produced, it may be readily granted that few of the arts are more intimately connected with chemistry, or depend more upon chemical laws, than dyeing.

Most of the recent improvements in dyeing have originated on the Continent; garancine, garanceux, with other preparations of madder, the application of albumen and caseine, and the introduction of murexide, picric acid, and modified archil colours, are all due to France; and the best shades of the red modification of the aniline colours have been produced in Vienna. The discovery of aniline dyes is, however, due to Mr. Perkin, who was the first to manufacture them in a practicable form. Fuchsine was discovered some months later by Verguin, who was the adapter of the discovery of Hofmann that bichloride of carbon gave a red colour with aniline. The number of colouring matters possessed by dyers is very limited; there is only one fast red upon cotton-madder, and only one fast blue-indigo. With regard to the artificial production of such substances as are formed by the vital activity of the plant from which madder is obtained (Rubia tinctorum), as alizarine, the most permanently active colouring principle of that substance has been produced by Messrs. Broenner and Messrs. Graebe and Liebermann. There can be little doubt that Graebe's alizarine will find many uses; its employment will be merely a question of cost. Concerning the state in which the colouring matters of madder exist in the plant, we know that alizarine is not contained as such in the root, but is formed by the action of acids or ferments on a glucoside whose chief properties and composition have been ascertained. That alizarine is the essential constituent of madder colours is proved by the fact that the finest and purest madder colours (Turkey red, madder pink, and purple) contain no other colouring matter in combination with the mordants; and there is little doubt that alizarine will form as efficient a substitute for madder as indigo has for woad. At the same time it does not follow that the other colouring matters of madder are useless.

All colours are produced indirectly by colouring substances, and owe their origin to light. We perceive objects and colours by means of rays of light proceeding from them to the visual organs. Light, as it proceeds from the sun, contains the elements of all colour, and can be analysed or decomposed by a glass or crystal prism, which will separate it into seven different hues. Only three of these appear essential, the others being produced by combinations of these three. The three primary colours are red, yellow, and blue, their union producing green, violet, orange, and indigo. The chemical substances, prussian blue and vermillion for instance, are not in themselves blue or red, but appear so because they possess the power of decomposing light. Prussian blue absorbs and destroys the red and yellow rays, leaving only the blue visible; while vermillion, on the contrary, nullifies the blue and yellow rays and reflects the red ones. It is the same with all colours; a colouring matter should be looked upon as a body having the power of reflecting undulations of a certain speed; colour cannot exist in solids, but it is an action of the undulations of the luminiferous ether on the organs of sight. All colours are alike in the dark; but they are not always the same in daylight as in artificial light. and chemical substances may change colour, or lose it altogether, without their chemical composition being affected. Effects of colour may be produced by light in two different ways, either by reflection from a surface which appears coloured—the more common phenomenon—or by transmission of light through a coloured transparent body, such as stained glass or liquid. Some substances vary in colour when seen by transmitted or reflected light; crystals of murexide are green by reflected and red by transmitted light, and there are a number of similar cases. This is an additional proof that colour is not due to a body itself, but to the position or physical arrangement of its particles.

It is not intended to enter into any other details of either physics or chemistry; numerous excellent works exist upon those subjects, and a brief resumé would necessarily be too incomplete to be of any real utility.

Water-Tests for Impurities.

This fluid is of no less importance from an industrial and manufacturing point of view than in its relations to man and the whole organic creation. Although it exists in great abundance and covers by far the largest part of the surface of our globe, it is never met with in a state of absolute purity it must be remembered that we are now considering water more especially in relation to dyeing and printing. Perfectly pure water, even if it could be obtained upon a large scale without much cost and trouble, would not in all instances answer the practical purposes of the dyer and printer. Experience teaches that in madder dyeing, for instance, especially with some preparations of that substance, the presence of carbonate of lime in water is considered to be very advantageous.

The following substances have been detected in natural waters: carbonic, nitric, nitrous, sulphuric, sulphurous, phosphoric, boracic, silicic, hydrochloric, and hydrosulphuric acids. The presence of the following basic substances, potassa, soda, lithia, ammonia, strontia, baryta, lime, magnesia, alumina, oxides of iron, manganese, zinc, copper, lead, silver, arsenic, nickel, and cobalt has been ascertained. Chlorine, bromine, iodine, fluorine, sulphur, and carburetted hydrogen have also been discovered in natural waters.

Nitrogen and oxygen, in varying proportions, are found in all waters. By far the greater number of the substances here mentioned occur, however, in very minute quantities, or are met with only under special conditions, as in the case of free sulphuric or hydrochloric acid, which is found in only a few cases, as in volcanic regions. Such metals as copper, zinc, lead, and others occur only in water pumped up from mines, or in isolated cases where small rivulets or springs happen to pass through lodes of metallic ore. The saying of Hippocrates concerning water—"Such as the soils are, so are the waters which run through them"—the result of patient and shrewd observation, is as true now as it was nearly twenty-five centuries ago. Water, as a general solvent, aided, moreover, by the mechanical effect of its motion, is capable of keeping not only in solution but also in suspension a large quantity of substances, among which organic matter holds a prominent place.

The mineral substances most frequently found in river, spring, and well water are as follows:—

Lime, combined with carbonic acid, mechanically suspended as chalk, or held in solution by an excess of carbonic acid or with other acids.

Magnesia occurs as carbonate of magnesia kept in solution in carbonic acid, and also as sulphate and chloride of magnesium.

Potash and Soda are never absent from natural waters, they are most frequently combined with chlorine, but also with sulphuric acid; in some, especially mineral waters so-called, they occur not unfrequently as carbonates.

Iron occurs in natural waters (mineral waters excepted) in only very small quantities, and generally as carbonate of the protoxide held in solution by carbonic acid; it is, however, by no means a rare constituent, as sulphate of the protoxide, in water discharged from mines and coal pits. When this water gets into rivers it is always precipitated by the constantly present alkaline substances in, one may say, all river waters.

Arsenious and Arsenic Acid have been detected in many of the natural waters of France and at baths in Germany in appreciable quantity; the latter very rarely, the former more frequently than is commonly supposed; these waters are used daily by a large number of the inhabitants of those countries, but without producing any apparently bad effect upon their health.

With the exception of organic matter, those substances in water which chiefly concern the dyer are lime, iron, and magnesia; the rest are of little importance. Lime occurs in water chiefly as carbonate and sulphate; when it is present as carbonate it is held in solution by carbonic acid, and as that gas is driven off when water is boiled it will of course become turbid, even if its original bulk, which should be measured previous to ebullition, be kept up as it should be by the addition of distilled water. Another and a better method of preventing the water losing bulk whilst boiling is to conduct the operation in a flask to which a long tube is attached, so that the steam may be condensed and caused to run back into the flask.

The ebullition should be kept up for some length of time, varying according to the quantity of water, but for not less than an hour, and the water will then be seen to become more or less turbid in proportion to the quantity of carbonate of lime contained in it. It may be easily rendered clear again by adding a few drops of hydrochloric or acetic acid, which dissolve the carbonate of lime with effervescence.

To enter into particulars concerning the analysis of water or the detection of the various salts which it may contain would consume too large a portion of our space; readers requiring further information on the subject will find it in works on analytical chemistry: it is here intended briefly to point out the different actions of the carbonate and sulphate of lime in dyeing. Both are injurious to bright colours, but not so to dark or sombre hues, unless present in very large quantity; carbonate of lime is even considered rather advantageous in madder dyeing, especially with certain kinds of madder, and ground chalk is frequently added to the water before using it, to make up any deficiency. Sulphate of lime in any quantity is injurious in dyeing with madder or with any dye procured from wood, causing waste of colouring matter with inferior results. The production of good brilliant light shades is incompatible with the use of water containing sulphate of lime. Magnesia in the state of chloride or sulphate does no harm provided it be not easily convertible into carbonate by boiling, which can readily take place should much carbonate of lime be present in the water; but if it should exist as carbonate or be converted into it during dyeing it is very detrimental, as it completely prevents the dyeing of certain colours and spoils the appearance of others. Madder, when mixed with one-fiftieth of its weight of calcined magnesia will not dye at all, and is spoiled by the addition of one part per cent. In the north of England it is sometimes present in quantity sufficient to affect madder colours; however, it is seldom present in water in sufficient quantity to be injurious.

Iron is found in almost all natural waters, but not usually in very large quantities, except in mineral waters. As has already been stated, it generally occurs as carbonate of the protoxide held in solution by excess of carbonic acid. Its presence, whether in large or small quantities, is very injurious to dyeing operations, and we therefore give a good practical test for its detection. If a single drop of tincture of logwood or strong logwood liquor be added to a wineglass of water perfectly free from iron, it will assume a sherry or claret colour, according to the quantity of lime present; but should the water contain iron, it will turn blue, blue-black, and finally inky-black, in proportion to the amount of that metal held in combination. This test requires to be examined immediately, for if the glass vessel in which it is made be left exposed to the air the logwood turns darker, and might perhaps be supposed to indicate iron in cases where none existed. Another precaution is necessary: the water to be tested should be freshly drawn, for should it have been standing for some time, even in well closed bottles, the iron is precipitated as insoluble oxide, in which case the change of colour by logwood no longer takes place. The influence of water impregnated with iron upon dyeing is very marked-pinks become drabs, and reds are turned into dull browns and chocolate colours, whilst, if the quantity of iron present be large, it combines with the colouring matters, and the cloth receives none of them, or only a small proportion. Fortunately for the dyers, the simple action of the oxygen of the air readily decomposes the salts of the protoxide of iron as met with in natural waters and turns them into peroxide of iron, so that water containing that metal need not necessarily be rejected for dyeing purposes. Where larger quantities of iron are present the same effect may be produced by aërating the water, and if possible heating it by means of waste

steam whilst standing in suitably-constructed vats. A precipitate of peroxide of iron is thus formed, insoluble in water and neutral or alkaline liquids. With the exception of mineral waters, properly so called, salts of potash and soda are seldom present as carbonates in sufficient quantity to produce any marked effect upon dyeing, whilst their existence as chlorides or sulphates is unimportant; and, moreover, the quantity of any of these salts usually found in water is but small. Silica is frequently met with in water, but is not usually considered to be injurious in dyeing. The experiments of Mr. O'Neill, of Manchester, tend to prove, however, that pure hydrated silicic acid is injurious in madder dyeing, although not strikingly so.

Organic Matter in water, that frightful bête noir to so many people, is by no means to be overlooked in its relations to dyeing and printing; it is especially detrimental to bleaching and clearing. Crenic and apocrenic acids, the various forms and modifications of humin, ulmin, and that series of substances which may be generalised as peaty matter, are often decidedly deleterious in either dyeing, bleaching, or clearing, imparting a yellow tinge not easily removable. These forms of organic matter may be tested for by mixing about a pint of the water with half a fluid ounce of a perfectly clear filtered solution of hypochlorite of lime (bleaching-powder), sp. gr. 1'014, and heating in a glass flask to about 160° F. (71° C.) Should the fluid so treated become yellow and precipitate a buff-coloured deposit, the water is unfit for clearing goods by the old method. It may, however, serve for clearing by the padding machine and steam box method, as that does not require nearly so much water. Dyeing and printing works are seldom so situated as to be able to use water without some purifying process. The most common purifying agents are exposure to air and light, and the separation of suspended matters by filtration; but there is one method to which we here call attention by which the worst water may be greatly improved even when largely impregnated with animal and vegetable matter. This consists in adding successively to each rooo cubic metres (=35,316 cubic feet, or 220,096 gallons) of water, which should be contained in a suitable tank, about 67 lbs. of dry perchloride of iron, and 186 lbs. of crystallised carbonate of soda, both previously dissolved in as pure water as can be obtained, to the volume of about 220 gallons (35 cubic feet). By this process most of the organic matter is removed, and some of the lime salts greatly lessened in quantity, being carried down with the flocculent sediment; this begins to fall slowly immediately after the addition of the iron and soda, which should be well mixed with the water by vigorous stirring. The chloride of sodium added by this process amounts only to and the too small a quantity to be in any way deleterious.

Water has not the same degree of solvent action upon all substances, and some remain insoluble under its influence; as a rule hot water dissolves more substance than cold, and does so more quickly, but the excess dissolved when hot frequently separates in crystals when cooled. This is a point which deserves notice, for a liquid which, when warm, is of the proper strength, may be too weak when cold. This happens very frequently with solutions of salts that are but moderately soluble, such as chlorate, bitartrate (so-called cream of tartar), and sulphate of potash. Crystallisation is also troublesome in steam colours, which though good enough when freshly made, become filled with small crystals on cooling, and work rough in the machine.

Boiler Incrustations.

As water is used for the production of steam a word may be said here concerning boiler incrustations. These are chiefly due to the salts of line (carbonate and sulphate) contained in water becoming deposited from it by evaporation and forming a hard stony crust inside the boilers. As the composition and quantity of mineral substances held in solution in water vary according to the water itself, it is obvious that no general specific against boiler incrustations can be given. The number of substances proposed for this purpose is too large to be enumerated; suffice it say that the action of some is simply mechanical, interposing such salts between the particles of the lime salts as will prevent their forming a solid crust, while others act chemically by bringing about double decomposition, and, lastly, several organic substances, such as sawdust, spent tan, potatoes, molasses, catechu, and others appear to act partly mechanically, partly chemically, although it is not possible to specify precisely how and why.

Rain water, which itself is too pure to give rise to these incrustations, cannot be used alone for boiler purposes, for it has been found to exert a highly corrosive action upon the iron plates and fittings. It can, however, be advantageously employed in conjunction with hard spring and river waters. and has the effect of diminishing the incrustation merely as the result of dilution. The drain pipes leading from the roof of the factory may be placed in connection with the tank or well from which the supply of water is drawn for the boilers. It will be seen hereafter that the same remedy is efficient both as a means of preventing incrustation and obviating corrosion, and that by using one of the alkaline substances about to be specified this twofold advantage may be secured. Iron will not rust when immersed in water containing a mere trace of caustic alkali, and it is a common observation that the iron vessels used in the preparation of potash and soda remain for any length of time free from all appearances of rust. This singular property is no doubt susceptible of important applications; amongst them may be mentioned the better protection of iron ships from the attack of bilge water, of hydraulic rams, smiths' tools, and other objects liable to be placed at times under the influence of water. Some forms of "surface condensers" become guickly corroded in consequence of the purity of the water accumulating in them by the process of distillation, and a small dose of caustic alkali is then useful as a means of protection; the engine cylinders are also to some extent preserved when alkaline anti-incrustation fluids are introduced into the boiler, for the minute quantity which is carried forward mechanically in the form of spray mixed with the steam suffices to preserve the iron; but a tendency to priming undoubtedly results from a too liberal use of soda or other alkali in the boiler. It will in practice be found easy to adjust the proportion of this ingredient so as to secure immunity from corrosion and incrustation, and at the same time avoid the tumultuous kind of ebullition known as "priming." In all cases it is advisable to carry out a rigid system of inspection, and it is only in the way of saving fuel and labour that the application of boiler-fluids is to be recommended.

Much benefit has often resulted from a coating of coal tar, or "dead oil," applied to the interior surfaces below the water line when the boiler is open

for cleaning and inspection. These will tend very considerably to lessen the adhesion of calcareous crusts, and are in no way affected by the boiler fluids in common use.

Soda crystals and caustic soda may be used with great success in boilers to effect the immediate precipitation of the lime salts, and they act by throwing down a finely divided form of carbonate of lime, which in turn furnishes nuclei for the deposition of subsequent accretions both of the carbonate and sulpliate, so that they are prevented from crystallising upon the walls of the boiler. A granular mud is thus formed, which subsides quickly, and may be for the most part got rid of through the "blow off" cock, which should be opened for this purpose two or three times every day, and run out with as little water as possible.

The use of caustic soda has undergone a thorough trial in the boilers of the Royal Arsenal, Woolwich, and we are enabled to give the following general instructions regarding its use, which are based upon an experience of upwards of ten years. The caustic soda should be dissolved in water so as to make a concentrated solution of sp. gr. 1300. This being perfectly miscible with water may be introduced into the boiler with the feed-water at any time when, from the pressure of steam, it may not be convenient to pass it through the safety-valve or other openings in the boiler. But when the steam is down there is no difficulty in introducing the prescribed dose by using a tin funnel with flattened aperture to pass it through the safety-valve, or a tubular arrangement with double cocks will answer at all times. Half a gallon per diem is the average quantity found sufficient for a 20-horse power stationary boiler working with Thames water for ten hours in the day. If the water should happen to be unusually hard a larger dose may be employed, but it would not be expedient to add in one charge more than the day's consumption. Locomotive and multitubular boilers have been worked successfully with caustic soda, and it is here that the importance of using anti-incrustation fluids makes itself most apparent.

CHAPTER II.

TEXTILE FIBRES AND TISSUES MADE THEREFROM. THICKENINGS AND PLASTIC MORDANTS.

BEFORE proceeding with an examination of those substances which serve to impart colour to woven tissues, we will devote a portion of our space to the study of textile fibres. Any substance capable of yielding a certain continuous and uninterrupted length of filamentary matter may be called textile fibre, and the number of such substances is large, but the proportion suitable for application to weaving purposes is limited, and only a few can be employed alone in the fabrication of tissue. Fibres are divided according to their origin into three groups—1. Mineral; 2. Vegetable; and 3. Animal. Up to the present time the artificial production of fibres has not succeeded, and those most useful to man are products of the vital activity of plants and animals.

Mineral Fibres.

The only mineral fibre we are acquainted with is asbestos or amianth, and although it cannot be dyed it may be interesting to refer briefly to it here. It is a polysilicate composed chiefly of lime, magnesia, and small quantities of alumina and iron. It is related to pyroxen; the percentage composition of the Tarantaise variety is expressed as follows:—Silica, 58·20; alumina, 0·14; protoxide of iron, 3·08; protoxide of manganese, 0·21; magnesia, 22·10; Lime, 15·55; water, 0·14. This variety is met with in very long, well-defined, glossy, and silky-looking filaments in that portion of the ancient Duchy of Savoy called La Tarantaise; the same variety also occurs in Corsica, where it was used by the celebrated philosopher Dolomieu for packing the minerals collected by him during his sojourn in that country.

Asbestos can be woven into tissues, especially if a flax fibre is worked up with it; its use is, however, very limited in the present day. The ancients who were in the habit of burning their dead used a tissue made of asbestos in order to collect the ashes of the dead bodies without admixture of the ash of the combustible used during the process of burning. The name "amianth," which signifies "undefiled"—that is, pure and unchangeable in the fire—has been given to it in consequence of its being incombustible. Tissues made of asbestos are at present practically used in Russia only. The fire brigade of St. Petersburg are provided with gloves and other portions of wearing apparel made of this substance in Siberia; it has also been used in the manufacture of paper in France and America.

Mineral Thickenings.

Only two mineral thickenings are at present employed, namely, kaolin and pipe-clay; these are generally used mechanically as resists. Pipe-clay and torrefied starch are employed to print complicated patterns, especially in block printing. The former is also used as a resist composition applied to parts of a fabric to prevent the deposition of colour or mordant upon those parts. By its use the quantity of gum required as a thickening is considerably reduced. Steam colours thickened with pipe-clay lose from 35 to 50 per cent of their intensity when applied to woollen tissues, but with cotton fabrics little loss is experienced. Before its use pipe-clay should be carefully washed and deprived of all coarse particles by being made to pass through a fine sieve, and then allowed to deposit slowly from water; it should be free from oxide of iron. Kaolin is used in a similar manner, but is more expensive.

Vegetable Fibres. Vegetable Thickenings.

The most important vegetable fibres, cotton, flax, hemp, aloe fibre, New Zealand flax (the fibre of the *Phormium tenax*), jute (also called Bengal hemp), ramé, woody fibre, and pine-apple fibre, are all composed chiefly of cellulose mixed with different foreign substances, sometimes called collectively incrustating matter. Under this term is included colouring matter and a peculiar substance possessing organised structure and known as suberine. As there exists a striking analogy between cellulose and vegetable thickenings, it is clear that an examination of the former leads directly to that of the latter.

Cellulose.

The study of the organs of plants teaches us that they are composed of a number of cells and hollow vessels varying greatly in form and shape. These vessels are all filled either with air, essential oils, starch, or an endless variety of organic and inorganic substances, among which may be instanced some peculiar active principles, sugar, fatty matter, and caoutchouc; but the main portion of plants, and the wood even of trees, consist of cellulose in a state more or less pure. This substance forms the connecting link between the animal and vegetable kingdom, for it also constitutes the cutaneous envelope and muscular system of the lowest form of animal life. As a type of perfectly pure cellulose we may take clean cotton fibre after it has been thoroughly bleached. In that state it is a colourless, inodorous, tasteless substance, insoluble in and not acted upon by water, alcohol, ether, benzol, &c. sp. gr. is equal to 1.525, water being 1.000; and its chemical composition may be expressed by the formula C6H10O5 or C12H20O10; it therefore belongs to the carbo-hydrates, or substances in which hydrogen and oxygen are contained in the proportion in which they exist in water. Pure cellulose may be heated to 446° without alteration, but if subjected to higher temperature it becomes brown-coloured and decomposed. When submitted to destructive distillation it yields water, carbonic acid, carburetted hydrogen, methylic alcohol, acetic acid, and creosote, with an abundant residue of porous charcoal. It burns readily with proper access of air, emitting but little smoke, and no particular smell. When perfectly pure or even nearly so, as in the form of well made paper, cellulose is quite indestructible by the action of

the air, but when mingled intimately with nitrogenised and especially albuminous substances, as in wood, the case is different. These substances are very prone to decompose, and when once their molecules are set in motion that motion is gradually imparted to the entire structure. The result is a slow combustion, which, assisted by air and moisture, soon destroys the substance, converting it by a series of metamorphoses, and by a process called by Liebig eremacausis, into a variety of organic compounds, including humin, ulmin, and humic and ulmic acids. According to M. Pasteur, the rotting of wood is due to the presence of infusoria which feed upon the albuminous substance contained in it; but as this theory has been the subject of much controversy we will not enter upon it here. Very dilute acids exercise no marked action upon cellulose even at boiling heat, but the action of concentrated acids is entirely different and very important from a practical point of view.

When pure cellulose, cotton for instance, after being thoroughly bleached, is placed in concentrated phosphoric or sulphuric acid at the ordinary temperature, it becomes disintegrated, and dissolves, colouring the acid. It changes into a viscous mass consisting of dextrine, which has the same chemical composition as cellulose; the only real change is, therefore, a molecular change. If the acid solution is largely diluted with water and then boiled, the dextrine fixes the elements of the water and is converted into glucose. If cellulose be treated with moderately diluted nitric, sulphuric, or hydrochloric acids and subject to the action of heat, disintegration occurs, and the result is a somewhat thickish mass apparently insoluble in water, and similar in its composition to cellulose. According to Dr. Calvert, of Manchester, an action almost as destructive as that of dilute mineral acids is exercised upon cotton and linen fibre by several organic acids. This statement led to some enquiries on the subject by M. A. Dollfus. The acids used were oxalic, tartaric, and citric, these being most often employed in printing calico, muslin, and other tissues. Pieces of very fine linen tissue and of muslin, after being thoroughly washed in distilled water, were steeped in aqueous solutions, each containing 2 per cent of vegetable acids. They were then dried in air, and exposed for one hour to respective temperatures of 176°, 212°, and 258.8°, with the results shown in Table I., p. 19.

Oxalic acid exerts a destructive influence equal to that of mineral acids. Among the pieces of tissue soaked in the acids aboved named, that which was steeped in oxalic acid assumed the darkest shade of brown, proving that the alteration is in direct proportion to the colouration.* Dr. Calvert's experiments made with solutions containing 4 per cent of water led to the results shown in Table II., p. 19. According to this author aqueous solutions of these acids containing 2 or 4 per cent act better when gum or gelatine is added to them in the proportion used for thickening, and the tissues exposed to the same temperature. The researches of M. Dollfus tend to prove the reverse, for in his experiments solutions containing 2 and 4 per cent of the acids and thickened with gum affected the tissue less than when no thickening was used. The action of acetic acid, even the glacial, is very slight; if a tissue be steeped in it and then dried scarcely any alteration takes place.

^{*}It is not improbable that part of the effect of the organic acids on cellulose may have been due to an admixture of traces of some mineral acid, such as sulphuric or nitric acid.

TABLE I.

Solution of oxalic acid at 2 per cent	Solution of citric acid at a per cent	Solution of tartaric acid at	Pure water	
oxalic	citric	tartaric	• • • • • • • • • • • • • • • • • • •	
acid	acid	acid	*	
at	at	· at	:	
Acted upon.	No action.	No action.	Linen. No action.	17
Acted upon.	Very feeble action.	Very feeble action.	Cotton. No action.	176° F.
Acted upon.	Very feeble action.	No action.	Linen. No action.	212
Acted upon.	Very feeble action.	Very feeble action.	Cotton. No action.	212° F.
upon.	Slightly acted upon.	No action.	Linen. No action.	258·8º F
upon.		upon.	No action.	

TABLE II.

Oxalic acid	Citric acid	Tartaric acid
:	:	*
:	:	*
:	•	
:		:
Both strongly acted upon.	Citric acid Both very feebly acted upon.	Linen. Cotton. Both slightly acted upon.
Both very strongly acted upon.	Both strongly acted upon.	Linen. Cotton. Both strongly acted upon.
Both entirely broken up.	upon. upon.	Linen. Cotton. Both strongly afted upon. Strongly afted Feebly afted

Dr. Calvert proposes to utilise the different action exercised by mineral acids upon vegetable and animal fibre as a means of distinguishing them in mixed When a piece of woven fabric, whose warp consists of cotton thread, is soaked in dilute sulphuric or hydrochloric acid and dried at 212°, the cotton thread is readily torn asunder, whilst the woollen thread remains as strong as before. This plan is applied on a large scale to worn-out fabric composed partially of wool, in order to recover the wool for use again in making similar fabrics or for working up into cloth. What is now known as vegetable parchment is made by soaking unsized paper (cellulose in the state of felt) for half a minute in concentrated sulphuric acid, and then washing it in large quantities of water, to the last of which ammonia has been added, when it assumes the aspect and consistence of an animal membrane. Gun-cotton consists of cellulose which has been acted upon by very strong nitric acid or by a mixture of concentrated sulphuric and nitric acids. An aqueous liquid containing ammoniacal solution of oxide of copper in sufficient quantity will dissolve cellulose, which can, however, be precipitated from it by acids without having suffered any chemical change, but with the entire loss of its organic structure. Gun-cotton is not soluble in this reagent, which is called from the name of its discoverer, Schweitzer's. Cellulose is blackened by fluoride of boron, but gun-cotton is not. Caustic and carbonated alkalies do not act upon cellulose even when warm, either in dilute or moderately strong solutions. According to M. Schwartz, cotton tissues placed in milk of lime are perceptibly weakened and deprived of their tensile strength unless they are kept from all contact with air. When submitted to the action of concentrated solutions of caustic alkalies either at the ordinary or a higher temperature, cellulose swells and becomes disintegrated. The action is, however, slow, especially with cellulose in a very compact and condensed form and free from incrustating matter, as, for instance, the so-called vegetable ivory (Phytelephas macrocarpa), an intrinsically pure and highly condensed form of cellulose. When a mixture of cellulose and a highly concentrated solution of caustic potash are heated in a pure silver basin to about 662°, a simultaneous formation occurs of formiate, acetate, and carbonate of potassa, with evolution of hydrogen gas and vapours of methylic alcohol (wood spirit). Chlorine gas and hypochlorous acid (hypochlorites, bleaching-powder) in a state of aqueous solution are not injurious to cellulose nor weakening to fibre, especially if not used at too high a temperature. In a more concentrated state and at a higher temperature chlorine and the above-mentioned preparations of it are highly deleterious, dissolving, burning, or destroying the cellulose entirely, and breaking up the fibre. According to Dr. Gladstone, cellulose will combine with caustic potassa, but water decomposes the combination, which is stable enough in absolute alcohol.

Having thus examined and pointed out the properties of cellulose, attention will next be turned to those kinds of vegetable fibre which are employed on a large scale, beginning with that one which is the most important of all from a manufacturing and commercial point of view, namely, cotton.

CHAPTER III.

COTTON.

THIS fibre is the product of a dicotyledonous plant or shrub belonging to the natural order of the Malvacea, and called Gossypium arboreum; the word cotton (French, coton) is of Arabian origin. Cotton is found principally in India, and was known and used there, as well as in Persia, Egypt, and Asia Minor, many centuries before the discovery of America, when it was found to be tolerably well known in that country also. Pliny mentions cotton as an Egyptian product, calling it xylon or gossypion. According to M. Ampère, jun., the microscopical examination of the wrappings of mummies show that woven cotton tissue was first used for that purpose about 80 A.D. In the year 1834,* James Thomson, F.R.S., instituted some interesting researches on this subject. He says:—

"My attention was attracted to the subject of Egyptian manufactures by the late Mr. Belzoni in the year 1822, during the exhibition of a model of the ancient tomb discovered by that enterprising traveller in Egypt. He had the goodness to present to me various specimens of cloth, chiefly from the mummies in his possession, one of which he had entirely denuded.

"On my remarking that these fabrics scarcely deserved the appellation of fine linen,' which from all antiquity had been bestowed on the linen of Egypt, and that the observations of Dr. Hadley, in the "Philosophical Transactions" for the year 1764, had thrown some doubt on the supposed fineness of this linen, he informed me that, during his researches in Egypt in those tombs and mummy-pits which he had explored, he had met with cloth of every degree of fineness, from the coarsest sacking to the finest and most transparent muslin, a fact which I subsequently found in a great degree confirmed by the acquisition of some interesting specimens of mummy-cloth sent to this country by the then Consul General of Egypt, the late Mr. Salt. The subject appearing to me sufficiently interesting to deserve investigation, and having collected a variety of specimens of cloth, my first care was to ascertain of what material they were made. This question had already engaged the attention of various enquirers and given birth to learned dissertations.

"Rouelle, in the "Memoirs of the French Academy of Sciences" for the year 1750; Larcher, the translator of "Herodotus," in the notes to that celebrated work; and the learned John Reinhold Foster, who wrote a tract "De Bysso Antiquorum," had all endeavoured to prove from their own examination

^{*} The London and Edinburgh Philosophical Magazine, vol. v., p. 355.

that the mummy-cloth of Egypt was cotton; and this opinion, on their authority, was adopted by the learned of Europe. It is singular that neither in the memoir of Rouelle, nor in the notes of Larcher, nor in the dissertation of Dr. Foster, in which this opinion is expressed, are any grounds assigned for, or any proofs given of, this opinion. The amount of their assertion is, that having examined the bandages of various mummies which are designated by them, and some of which I have myself since carefully examined, they found all those which were free from resinous matter to be cotton. I am forced to confess that, with all the attention I could bestow upon them, and with the assistance of various intelligent manufacturers, I was unable to arrive at such a conclusion. Some were of opinion that the cloth was cotton; others that it was linen; and some, again, that there were in the collection specimens of both—a proof that our means of judging were unworthy of confidence.

"The great difference in the specific gravities, as well as in the conducting power of linen and cotton, is sufficient to enable us, by careful experiments, to discriminate accurately between them; and there are few individuals who have been accustomed to the use of both cotton and linen who cannot readily distinguish, by that delicate sense of touch diffused over the whole body, between the two fabrics; but such tests require much larger portions of the material than I had at my disposal, many of the specimens submitted to my examination not being larger than a shilling. I found the difference of smell in the burnt fibres, and the degree of polish which each kind of cloth took on being rubbed with a glass stopper, as well as other empirical modes suggested to me, liable to great uncertainty, and I sought in vain for any chemical test. It occurred to me that the supposed unfitness of cotton lint, compared with linen, for dressing wounds had been accounted for by the different form of their fibres, the one being sharp and angular and the other round and smooth; and, in fact, I found, in the 12th volume of the "Philosophical Transactions," for the year 1678, this structure ascribed to them by that early microscopic observer, M. Leuwenhoek. It seemed to me, therefore, that the most simple mode of distinguishing between cotton and linen would be to subject the fibres to examination under a powerful microscope. Not being possessed of such an instrument, nor accustomed to its management, my friend Mr. Children undertook, through Sir Everard Home, to solicit the assistance of M. Bauer, whose labours are well known to the scientific world, and whose microscopic drawings have for a series of years enriched the "Transactions of the Royal Society." I transmitted to him various fibres of cotton and linen, both manufactured and in their raw state, as well as fibres of unravelled munimy-cloth, and in a few days I received from him a letter in which he pronounced every specimen of mummy-cloth subjected to his examination to be linen. This letter was accompanied by a beautiful drawing, exhibiting the fibres of both raw and unravelled cotton as flattened cylinders, twisted like a corkscrew, whilst the fibres of linen and various mummy-cloths were straight and cylindrical.

"Repeated observations having established beyond all doubt the power of the microscope accurately to distinguish between the fibres of cotton and linen, I obtained, through the kindness of various individuals connected with the British Museum, the Royal College of Surgeons, the Hunterian Museum of Glasgow, as well as other public institutions both at home and abroad, a great variety of cloths of human mummies, and of animals and birds, which, being subjected to the microscope of M. Bauer, proved without exception to be linen;

nor has he, amongst the numerous specimens we have both collected during many years, been able to detect a single fibre of cotton, a fact since recently confirmed by others, and proving incontestably that the mummy-cloth of Egypt was linen.

"The filaments of cotton, when viewed through a powerful instrument, such as the improved achromatic microscope of Ploessl, of Vienna, which, for magnifying power and clearness of vision, M. Bauer has found superior to every other he has had an opportunity of using, appear to be transparent glassy tubes flattened and twisted round their own axis. A section of the filament resembles in some degree a figure of 8, the tube, originally cylindrical, having collapsed most in the middle, forming semi-tubes on each side, which give to the fibre, when viewed in certain lights, the appearance of a flat ribbon with a hem or border at each edge. The uniform transparency of the filament is impaired by small irregular figures, in all probability wrinkles or creases, arising from the desiccation of the tube. The twisted and corkscrew form of the filament of cotton distinguishes it from all other vegetable fibres, and is characteristic of the fully ripe and mature pod, M. Bauer having ascertained that the fibres of the unripe seed are simple untwisted cylindrical tubes, which never twist afterwards if separated from the plant; but when the seeds ripen, even before the capsule bursts, the cylindrical tubes collapse in the middle and assume the form already described.

"This form and character the fibres retain ever after, and in that respect undergo no change through the operation of spinning, weaving, bleaching, printing, and dyeing, nor in all the subsequent domestic operations of washing, &c., till the stuff is worn to rags; and then even the violent process of reducing those rags to pulp for the purpose of making paper effects no change in the structure of these fibres. 'With Ploessl's microscope,' says M. Bauer, 'I can ascertain whether cotton rags have been mixed with linen in any manufactured paper whatever.'

"The elementary fibres of flax (*Linum usitatissimum*) are also transparent tubes, cylindrical, and articulated or jointed like a cane. This latter structure is only observable by the aid of an excellent instrument.

"Of the productions of the loom amongst the nations of antiquity, with the exception of those which form the subject of this paper, we know only what is to be gathered from the few scattered notices in ancient writers. Even the great work of Pliny, the encyclopædia of that day, and, with all its defects, an invaluable collection of facts, affords but scanty information. Of the manufactures of the Egyptians and of their domestic arts our knowledge is more ample, but we are more indebted to their monuments than to their historians; and the paintings which adorn their tombs, and which are fresh at the present day as from the hand of the artist, have revealed to us more than all the writers of antiquity.

"Of the products of the Egyptian loom, however, we know scarcely more than the mummy-pits have disclosed to us; and it would be as unreasonable to look through modern sepulchres for specimens and proofs of the state of manufacturing art amongst ourselves as to deduce an opinion of the skill of the Egyptians from those fragments of cloth which envelope their dead, and which have come down, almost unchanged, to our own time. The curious or costly fabrics which adorned the living, and were the pride of the industry and skill of Thebes, have perished ages ago. There are, however, amongst these

remains some which are not unworthy of notice, which carry us back into the workshops of former times, and exhibit to us the actual labours of the weavers and dyers of Egypt more than two thousand years ago.

"The great mass of mummy-cloth employed in bandages and coverings, whether of birds, animals, or of the human species, is of coarse texture, especially that more immediately in contact with the body, and which is generally impregnated with resinous or bituminous matter. The upper bandages nearer the surface are finer. Sometimes the whole is enveloped in a covering coarse and thick, and very like the sacking of the present day; sometimes in cloth coarse and open like that used in our cheese-presses, for which it might easily be mistaken. In the College of Surgeons are various specimens of these cloths, some of which are very curious.

"The beauty of the texture and peculiarity in the structure of a mummycloth given to me by M. Belzoni was very striking. It was free from gum or resin, or impregnation of any kind, and had evidently been originally white. It was close and firm, yet very elastic. The yarn of both warp and woof was remarkably even and well spun. The thread of the warp was double, consisting of two finer threads twisted together. The woof was single. The warp contained ninety threads in an inch; the woof, or weft, only forty-four. The fineness of these materials, estimated after the manner of cotton yarn, was about thirty hanks in the pound. The subsequent examination of a great variety of mummy-cloths showed that the disparity between the warp and woof belonged to the system of manufacture, and that the warp generally had twice or thrice, and not seldom four times, the number of threads in an inch that the woof had. Thus, a cloth containing 80 threads of warp in the inch, of a fineness of about 24 hanks in the pound, had 40 threads in the woof; another, with 120 threads of warp of 30 hanks, had 40; and a third specimen only 30 threads in the woof. These have each, respectively, double, treble, and quadruple the number of threads in the warp that they have in the woof. This structure, so different from modern cloth, which has the proportions nearly equal, originated probably in the difficulty and tediousness of getting in the woof when the shuttle was thrown by hand, which is the practice in India at the present day, and which there are weavers still living old enough to remember the universal practice in this country.

"I have alluded to some specimens of mummy-cloth sent to this country by the late Mr. Salt. I am unacquainted with their history or origin further than that they were brought from Thebes, and were contained in the outer packing-case of a mummy now in the British Museum. They were evidently the spoils of some other mummy, but when and where opened I have in vain endeavoured to learn. There were various fragments of different degrees of fineness, some fringed at the ends and some striped at the edges. They merit a more particular description.

"My first impression on seeing these cloths was that the finest kinds were muslin, and of Indian manufacture, since we learn from the "Periplus of the Erythrean Sea," ascribed to Arrian, but more probably the work of some Greek merchant himself engaged in the trade, that muslins from the Ganges were an article of export from India to the Arabian Gulf; but this suspicion of their being cotton was soon removed by the microscope of M. Bauer, which showed that they were all, without exception, linen.

"Some were thin and transparent and of very delicate texture. The finest

appeared to be made of yarns of near 100 hanks in the pound with 140 threads in the inch in the warp, and about 64 in the woof. A specimen of muslin in the Museum of the East India House, the finest production of the Dacca loom, has only 100 threads in an inch in the warp, and 84 in the woof; but the surprising fineness of the yarns, which, though spun by hand, is less than 250 hanks in the pound, gives to this fabric its unrivalled tenuity and lightness. Some of the cloths were fringed at the ends, and one, a sort of scarf about 4 feet long and 20 inches wide, was fringed at both ends. Three or four threads twisted together with the fingers to form a strong one, and two of these again twisted together and knotted at the middle and at the end to prevent unravelling, formed the fringe, precisely like the silk shawls of the present day.

"The selvedges of the Egyptian cloths generally are formed with the greatest care, and are well calculated by their strength to protect the cloth from accident. Fillets of strong cloth or tape also secure the ends of the pieces from injury, showing a knowledge of all the little resources of modern manufacture. Several of the specimens, both of fine and coarse cloth, were bordered with blue stripes of various patterns, and in some alternating with narrow lines of another colour. The width of the patterns varied from half an inch to an inch and a quarter. In the latter were seven blue stripes, the broadest about half an inch wide nearest the selvedge, followed by five very narrow ones, and terminated by one an eighth of an inch broad. Had this pattern, instead of being confined to the edge of the cloth, been repeated across its whole breadth, it would have formed a modern gingham, which we can scarcely doubt was one of the articles of Egyptian industry. A small pattern about half an inch broad formed the edging of one of the finest of these cloths, and was composed of a stripe of blue followed by three narrow lines of the same colour, alternating with three lines of fawn-colour, forming a simple and elegant border. These stripes were produced in the loom by coloured threads previously dyed in the yarn. The nature of the fawn-colour I was unable to determine. It was too much degraded by age, and the quantity too small, to enable me to arrive at any satisfactory conclusion. Though I had no doubt the colouring matter of the blue stripes was indigo, I subjected the cloth to the following examination :- Boiled in water for some time, the colour did not yield in the least, nor was it at all affected by soap nor by strong alkalies. Sulphuric acid, diluted only so far as not to destroy the cloth, had no action on the colour. Chloride of lime gradually reduced, and at last destroyed it. Strong nitric acid dropped upon the blue turned it orange, and in the same instant destroyed it. These tests prove the colouring matter of these stripes to be indigo.

"This dye was unknown to Herodotus, for he makes no mention of it. It was known to Pliny, who, though ignorant of its true nature and the history of its production, has correctly described the most characteristic of its properties, the emission of a beautiful purple vapour when exposed to heat. Had his commentators been acquainted with the sublimation of indigo it would have saved many learned doubts. We learn from the "Periplus" that it was an article of export from Barbariké on the Indus to Egypt, where its employment by the manufacturers of that country, probably from a remote period, is clearly established by the specimens here described.

"Amongst the various cloths for which I am indebted to the curators of the Hunterian Museum at Glasgow, is one of a pale brick or red colour. My

attention was lately recalled to this specimen by observing a similar colour in the outer coverings of two fine mummies presented to the University of London by Mr. Morrison, one of which has been recently unrolled. Having obtained specimens of both, I subjected them, with that from Glasgow, to the following experiments:-Treated with cold water the colour was not affected. Boiling distilled water in a few minutes nearly removed the whole. Diluted sulphuric or muriatic acid had no action on it; but a feeble alkali, whether carbonated or caustic, destroyed the colour immediately. Examined with a lens, the specimens from Glasgow exhibited small distinct grains or concretions, of a red colour, disseminated through the fibres of the cloth. Notwithstanding the fugitive nature of the colouring matter of safflower, the Carthamus tinctorius of botanists, I am strongly disposed to consider the three specimens here examined as having been dyed with that plant. The small granular particles of a red colour observed in the Glasgow specimen are sometimes found in cloth dyed with Carthamus. There is also in the covering of the mummy of the London University, which is unstripped, a rosy hue peculiar to this dye. The resistance of the colour to acids, and its instant yielding to the weakest alkalies, is characteristic of safflower. Lastly, Carthamus has long been an article of cultivation in Egypt, and the first processes employed by the European dyers were derived, with the dye itself, from that country, where, in all probability, it has been cultivated and used for ages, and is to this day an article of considerable export.

"In the Glasgow mummy there was, moreover, a narrow slip of cloth about four inches broad, extending from the crown of the head to the feet, of a yellowish colour, of which portions were still fresh. On examination, no mordant appeared to have been used to fix this dye, and washing in cold water greatly impaired it. Comparative experiments made on this colour, and on that afforded by Carthamus to simple water before the pink dye is extracted, left little doubt of their being identical. They were slightly and similarly affected by solutions of alumina and of iron, and appeared to have very feeble affinities for either vegetable fibre or any of the earthy or metallic bases.

"Though the age of mummies from which these specimens were derived has not been ascertained, yet we may fairly presume that it goes back to a period so far remote as to make the preservation so long, of delicate and fugacious colouring matter like Carthamus, or even the more permanent one of indigo, very surprising, and proves that substances which readily yield to the combined and destructive agency of heat or light and moisture are almost unalterable when secured from the action of the latter. Portions of the blue cloth which had resisted in the dark and dry sepulchres of Thebes for ages lost,

by a few days' exposure on the grass, nearly all their colour.

"Mummy-cloth not stained or discoloured by resin or bitumen is generally of a pale brown or fawn colour, which has been supposed to arise from some astringent preparation employed by the Egyptians for its preservation. All this cloth imparts to water a brown colour, in which I have sought in vain for any trace of tannin. In none of the specimens I have examined did either gelatine or albumen, or solutions of iron, afford any precipitate; but the subacetate of lead produced a cloud, indicating the presence of extractive matter. I am inclined to think that, if astringent matter has been found, it is in those bandages which have received a preparation of gum or resin, and which are distinguished from the others by their stiffness. These I have not examined.

All these cloths, whether fine or coarse, are more or less rotten. Of the numerous specimens which have fallen under my notice, the outer covering of the fine mummy in the London University has suffered least; it is comparatively sound. Whether this be an argument against its high antiquity I know not, but the cloth is evidently ancient Egyptian; nor is it, I believe, pretended that in those factitious mummies manufactured by the Arabs, of which several were found by Blumenbach in the British Museum, the bandages and envelopes are not genuine. Of the ancient cloth, there is such an accumulation in the mummy-pits and sepulchres of Egypt as to have become a subject of speculation in Europe for the purpose of making paper. The inquiries, therefore, which form the subject of this communication are not affected by any question of the integrity of those mummies from whence the specimens were derived, of which, however, no doubt is entertained.

"The period during which the custom of embalming prevailed in Egypt embraces a long succession of ages. From the first of the Pharaohs to the last of the Ptolemies, with whom this ancient right is supposed to have become almost extinct, chronologists reckon more than twenty centuries during which the art was practised which has handed down to us these scanty remains of Egyptian industry, the only vestiges of the labours of the ancient loom now in existence. They prove the arts of spinning and weaving flax to have attained a high degree of perfection, many of the specimens of mummy-cloth here described being of a quality to excite admiration even at the present day, and the finest of these fabrics approaching in excellence our delicate muslins. The coloured borders establish the fact of indigo having been known and used as a dye in Egypt from a remote era.

"During this long period industry and the arts of life connected with civilisation must have made considerable progress, which we shall, however, remain unable satisfactorily to trace till more accurate knowledge of the ancient language and characters of the Egyptians shall have interpreted the dates and fixed the chronology of their monuments and paintings. In the tomb of Beni Hassan is a representation of a loom (figured in Count Minutoli's travels) of such primeval simplicity as to resemble the first rude efforts of savage art to form a web such as Don Ulloa in his voyages has described as used by the native Indians of South America. Between this loom and that in which the corslet of Amasis was woven, mentioned by Herodotus, and more particularly described by Pliny, the distance is immense.

"It is not improbable that future researches directed to this object may discover, in the ancient sepulchres and mummy-pits, fragments of cloth, now trodden under foot and unheeded by the traveller, which would throw much light on the interesting subject of ancient manufactures.

"The question debated amongst the learned of the nature of the Byssus of the ancients, I may in conclusion be permitted to observe, appears to me to be finally settled by the present communication. Herodotus states that the Egyptians wrapped their dead in cloth of the Byssus. It has been shown that, without exception, every specimen of mummy-cloth yet examined has proved to be linen. We owe, therefore, the satisfactory establishment of the fact, that the Byssus of the ancients was FLAX, to the microscope of M. Bauer."

The cotton shrub grows only in the warmer (tropical and sub-tropical) portions of the globe. The most important varieties are the Gossypium arboreum and Gossypium herbaceum. The Gossypium herbaceum is generally

cultivated at Malta, in Sicily, in Syria, and other portions of the Levant, and in the islands of the Greek Archipelago. At Malta and Sicily this plant is herbaceous and annual, but in warmer climates it becomes a perennial shrub growing to the height of about 7 or 9 feet. The Indian cotton shrub is a sub-species of the foregoing, but is perennial. The Gossypium arboreum is a tree which attains a height of about 15 or 18 feet. It is cultivated in India, Arabia, China, the Canary Islands, and especially in the United States of America.

The fruit of the cotton tree consists of a capsule containing from three to five valves, and as many divisions holding a number of seeds. These seeds are each surrounded by a flock of cotton, which becomes swollen when the seed reaches maturity, and the valves consequently open. The cotton gathering takes place in August, September, or October, according to the climate. The shells of the fruit are left on the tree, but the cotton and the seeds are pulled off, and after being dried in the sun are separated from each other by a machine known either as the roller gin, the Macarthy gin, or the saw gin.

The quality of the cotton is judged by the length of its fibres, long ones being about 1 inch (from 2 to 4 centims.) in length, and short ones about 1 an inch (from 1.5 to 2 centims.) The United States produce the best kinds of both these varieties. The cotton grown in Algeria and Brazil is all of the

long kind. India and the Levant produce both varieties.

Cotton filaments or fibres when fully ripe but not dried exhibit under the microscope a membranous hollow tube of cylindrical shape, and closed at both ends. When dry this cylinder becomes flattened and twisted, and assumes a ribbon-like shape rather thicker at the edges than in the middle. Its largest diameter is about 0.03037 of a millimetre, but it tapers off cylindrically at both ends; on examination with a lens magnifying 400 times no opening whatever is seen inside the walls of the cylindrical cell, but it is nevertheless permeable by liquids. According to the late Mr. Walter Crum, the examination of sections of cotton fibres taken perpendicularly to their length proves that they are nearly solid: some of these sections are of a cylindrical shape, but the greater part are irregularly oblong or oval, bearing some likeness to the fibres of flax and hemp. According to M. Alcan, the author of a French treatise on cotton spinning, the peculiar action of cotton upon concentrated aqueous solutions of caustic soda and potash was first discovered and pointed out by the late M. Persoz. Mr. John Mercer, however, turned this discovery to practical use, and patented a process known as Mercerising. By this process the woven tissue is immersed for a few minutes only in a solution of caustic soda (sp. gr. 1.250), and immediately afterwards well washed in plenty of cold water, after which it is passed through an acid bath. The result is contraction of fibre, the threads becoming rounder, firmer, and closer together, the loss in length and breadth to the material being about 1-15th each way. Cotton tissue thus treated has an especial affinity for some colours, especially for indigo-blue. The process has, however, been abandoned on account mainly of the expense of the soda, which was not justified by the results obtained. M. Daniel Keechlin-Schouch, of Mulhouse, was the first to call the attention of dyers and printers to the occasional occurrence in cotton fabrics of fibres which resist the dye and remain white; this was attributed by him to non-maturity of the fibre, a surmise which was confirmed by the experiments of Mr. Walter Crum. These so-called dead fibres when examined with a microscope were found to be of such very thin texture as to be almost invisible except at the edges; they are nearly twice as wide as ordinary ripe cotton, and contain a larger number of longitudinal and transverse folds. This dead cotton is not equally conspicuous with all dyes; it is very apparent with indigo and madder-pink, but not so with safflower and deep madder-red.

For the benefit of those to whom the "Memoirs of the Literary and Philosophical Society of Manchester" may not be conveniently accessible, we abridge from the fourth volume of the third series some of the interesting and highly valuable researches of Dr. Schunck, F.R.S., "On some Constituents of the Cotton Fibre."

Dr. Schunck's endeavour was to throw a little more light on the nature of the substances which are contained in or attached to the framework of cellulose of which cotton fibre mainly consists, and which are, together with the latter, produced by the plant, without taking into consideration the foreign and extraneous matters introduced during the process of manufacture. It is well known that these substances are almost insoluble in water, but soluble in hot alkaline lye. Indeed the principal operation in the bleaching of cotton goods consists in subjecting them for some time to the action of boiling solutions of soda or some other alkali—chlorine or its compounds being only used to impart to them the highest degree of whiteness. Dr. Schunck confined himself in this investigation to those natural constituents of cotton fibre which are insoluble in water, but soluble in alkaline lye, and which are afterwards precipitated from the alkaline solution by acid. He employed cotton-yarn made from definite unmixed kinds of cotton. Apart from financial considerations, yarn presents certain advantages as compared with raw cotton. It is much freer from mechanical impurities, which are to a great extent removed during, or rather previously to, the operations of spinning; while, on the other hand, in a well-ordered manufactory, little or nothing of a foreign nature is added to the cotton to render it impure. It can also be treated without any trouble, and in large quantities, in the ordinary vessels used by bleachers, without rendering it necessary to set up special apparatus for the purpose.

In the first experiment, 450 lbs. of No. 20 yarn, carefully spun from East Indian cotton, of the variety called "Dhollerah," was treated, in an ordinary bleacher's kier heated by steam, with boiling water containing 131 lbs. of sodaash for seven and a half hours. The resulting dark brown liquor, after the yarn had been taken out, drained, and slightly washed, was removed into another vessel and mixed with an excess of sulphuric acid, which produced a copious, light brown, flocculent precipitate, while the liquid became nearly colourless. This precipitate was allowed to settle; the liquid was poured off, and, after being washed with cold water to remove the sulphate of soda and excess of acid, the precipitate was put on strainers of calico and allowed to drain-an operation which, in consequence of its gelatinous nature, occupied some time. A thick pulp was thus obtained, which was found to weigh 60 lbs. Of this 3 lbs. was taken and dried completely, at first in a stove and then in a water-bath, when it left 531 grs. of a brown, brittle, horn-like substance, translucent at the edges. The whole of the precipitate, if dried, would therefore have weighed 10,620 grs., which is equal to 0.337 per cent of the weight of the cotton; that is to say, 1000 lbs. of cotton-yarn would have yielded nearly 3½ lbs. of matter insoluble in water, but soluble in alkali. This result is, of course, only approximative.

In a second experiment 2400 lbs. of yarn, made from the same kind of cotton, but of rather inferior quality, was treated in the same way; but the quantity of precipitate obtained was not determined.

The third experiment was made with 500 lbs. No. 20 yarn, spun from American cotton of the kind called in commerce "Middling Orleans." It was treated in the same manner as the other two lots, and yielded a precipitate of exactly the same appearance as that from East Indian cotton, and amounting, when dry, to 0.48 per cent of the weight of the yarn employed.

The precipitate in all three cases consisted for the most part of organic matter. In addition to the matter extracted from the cotton by the alkali, it contained a small quantity of cotton filaments, which had been detached from the yarn during the process of boiling. When incinerated, it left from 2.3 to 6.9 per cent of a light yellow non-alkaline ash. This ash consisted chiefly of oxide of iron, alumina, and silicate of alumina, the remainder being sulphate of lime and sulphate of soda.

The three lots of precipitate obtained were treated separately; but as the products which they yielded were essentially the same, the same process of

treatment was applied to all. This process was as follows:-

The precipitate was in the first instance treated, while still moist, with boiling alcohol, and the boiling liquid was filtered through a large tin funnel, surrounded by hot water. The residue on the filter was treated again with boiling alcohol, and the process was repeated until nothing more was dissolved. More than half of the precipitate remained undissolved. The undissolved residue was much paler than the original precipitate, the colouring material of which had, for the most part, passed into solution. The alcoholic liquid, which was of a dark brown colour, deposited, on cooling, a quantity of dirty white flocks, which were filtered off, washed with alcohol, and then re-dissolved in boiling alcohol. On adding to this solution a little acetate of lead, a dark brown precipitate was produced, consisting of a compound of colouring matter with lead; and the liquid, after being filtered as before through a hot water funnel, and allowed to cool, deposited a quantity of nearly white flocks. These were filtered off, washed with alcohol to remove the excess of lead-salt, and then treated with boiling dilute caustic soda-lye, in which they melted like wax or fat, without dissolving. The mass, after cooling, was filtered off, washed with water, and then dissolved again in boiling alcohol, to which a little animal charcoal was added. The solution, which was quite colourless, deposited, after filtration and cooling, a quantity of crystalline scales, of a beautiful pearly lustre, and generally in such abundance as to convert the liquid into a thick jelly. This deposit, which was at first very bulky, on being filtered off and dried, shrank considerably, and yielded at last a white or faintly yellow wax-like cake, consisting of a body termed by Dr. Schunck Cotton Wax.

The alcoholic liquid from which this substance was deposited was of a dark brown colour. It contained two bodies, which, for want of a better term, may be called colouring matters, and also a small quantity of a crystalline fatty acid having the properties and composition of margaric acid. The two colouring matters resemble one another in most of their properties, but may

be distinguished by their different degrees of solubility in alcohol—one being easily soluble in cold alcohol, the other soluble in boiling, but very little soluble in cold alcohol. As these substances possess very few characteristic properties, and it is doubtful whether they are peculiar to cotton or not, the one which is most easily soluble in alcohol is called simply Colouring matter A, the other Colouring matter B. These bodies were separated from one another and from the fatty acid in the following manner:- The liquid having been evaporated, left a brown, semi-solid, resinous mass, which was treated with a small quantity of warm or boiling alcohol. This dissolved only a part of the mass, the remainder being left undissolved as a brown powder, consisting for the most part of the colouring matter B. The liquid having been filtered, the powder was treated with a large quantity of boiling alcohol, in which it usually dissolved almost entirely. A small quantity, however, of a brown flocculent substance was generally left undissolved; and this substance, which consisted of impure pectic acid, having been filtered off while the liquid was hot, the latter, on cooling, deposited the greatest part of the colouring matter as a brown powder, which only required to be filtered off, washed with alcohol, and dried. The dark brown alcoholic liquid, containing the more soluble colouring matter A, as well as the fatty acid and a portion of the colouring matter B, was now mixed with ammonia and chloride of barium, which gave an abundant greyish brown precipitate, consisting of all the organic matter previously contained in the liquid in combination with baryta. This precipitate was filtered off, and then treated with boiling alcohol. The latter being filtered boiling hot, afforded, on cooling, a small quantity of a brownish crystalline deposit. This process was repeated as long as the filtered liquid deposited anything, and until, therefore, the precipitate was thoroughly deprived of everything soluble in alcohol. The crystalline matter deposited from the alcoholic liquid consisted almost entirely of the baryta salt of the fatty acid. After being filtered off it was treated with warm dilute hydrochloric acid, by which it was decomposed, the fatty acid rising to the surface as a light brown oil, which became solid on cooling. The latter, after being well washed with hot water, was dissolved in warm alcohol, and the solution, having been decolourised with animal charcoal and filtered, was evaporated spontaneously, when it left a perfectly white mass of crystalline needles, consisting of the fatty acid in a state of purity.

The baryta-precipitate, after treatment with boiling alcohol, was decomposed with warm dilute hydrochloric acid, which left undissolved a dark brown, semi-fused mass. This mass, after being kneaded in hot water and thoroughly freed from barium salt, was treated with boiling alcohol. The alcohol generally left some brown powder undissolved, consisting of colouring matter B; and an additional quantity was usually deposited from the alcohol on cooling. Having been filtered off, it was purified by dissolving it in a sufficient quantity of boiling alcohol, as above described. The filtered liquid left, on evaporation, a dark brown resinous mass, which was reduced to a fine powder, and then agitated in a flask with ether. The ether dissolved only a very small portion of the mass, but it served to remove a trace of fatty acid contained in it. The ether, on evaporation, left a brown fatty residue, which, after combination with baryta and treatment of the compound with boiling alcohol, as just described, yielded a quantity of pure fatty acid. The portion left undissolved

by the ether was treated with cold alcohol, which dissolved the greatest part of it. The dark brown solution, after being filtered from a small quantity of colouring matter B, which was usually present, was evaporated to dryness, when it left a dark brown, shining, resin-like residue, consisting of the colouring matter A.

The greatest part of the precipitate produced by acid in an alkaline extract of cotton is insoluble in alcohol. This portion, when dry, has the appearance of a brown, friable, earthy mass, among which cotton filaments, particles of woody fibre, and other impurities derived from the cotton may be seen. When burnt it leaves a considerable quantity of ash. Its weight, when dry, amounted, in the case of East Indian cotton, to 77 per cent of that of the entire precipitate, in that of American cotton to 66 per cent. Though much lighter in colour than the precipitate before treatment with alcohol, it still contains a quantity of colouring matter, which cannot be extracted by means of boiling alcohol, not even when ammonia is added—a circumstance which is due either to the presence of some colouring matter distinct from those just referred to, or perhaps to the latter being intimately combined with, or firmly attached to, some other constituent of the mass. Dr. Schunck supposes that it contains also a small quantity of some albuminous substance, the presence of some such substance being rendered probable by an examination of the products of decomposition with caustic alkali, as will be explained presently. Its chief constituent, however, is a body belonging to the pectine class, generally either pectic or parapectic acid, or a mixture of both. The presence of some such body is indicated by the gelatinous appearance of the precipitate with acid, its increasing in bulk and partially dissolving in water after the precipitating acid has been removed, and its shrinking and curdling on the renewed addition of acid or of salts or alcohol. Nevertheless the isolation and preparation, in a state of purity, of this substance cannot be effected without considerable difficulty, in consequence of the pertinacity with which the colouring matter adheres to and accompanies it. If the precipitate, after exhaustion with boiling alcohol, is treated with boiling water, the latter dissolves a considerable quantity of the body in question, but on evaporation it leaves a dark brown residue, which, on analysis, is found to contain no inconsiderable amount of nitrogen, a proof of the presence of one or both of the colouring matters of cotton. Dr. Schunck was unsuccessful in his attempts to remove this impurity by means of animal charcoal, earths, metallic oxides, or salts of any kind. He succeeded, however, in devising two methods of preparing, in a state of tolerable purity, a body soluble in water having the properties and composition of Frémy's parapectic acid, and thus proving that cotton contains a substance belonging to the pectine series. He was unable to procure pectine itself, though there can be little doubt that it is pectine which exists originally in the fibre and gives rise to the formation of the pectic and parapectic acids which are contained in the alkaline extract. One of the methods employed for preparing this acid, founded on the insolubility of its alkaline compounds or salts in an excess of caustic alkali, was as follows:-

The precipitate from the alkaline extract of cotton, after exhaustion with boiling alcohol, was, without being previously dried, dissolved in dilute caustic soda-lye. The solution, after being filtered in order to separate the filaments of cotton and other impurities which were present, was mixed with alcohol,

which produced an abundant light brown flocculent precipitate, consisting of impure pectate and parapectate of soda. The liquid, which was brown, contained a considerable quantity of colouring matter, and was filtered. The precipitate, after being washed with alcohol, was again dissolved in water, and to the solution there was added a quantity of strong caustic soda-lye, which produced a precipitate of a much paler colour than that with alcohol, while the liquid retained in solution another portion of colouring matter. The precipitate having been allowed to settle, the liquid was decanted, and the precipitate was stirred up with a fresh quantity of caustic soda-lye, the process being repeated until the supernatant liquid had become colourless. The precipitate was now treated with warm dilute hydrochloric acid, which took up the alkali, leaving a quantity of pale brown flocks undissolved. These were filtered off and washed for some time with cold water, the latter being exchanged for alcohol as soon as the principal part of the acid and chloride of sodium had been removed, in order to prevent a loss of parapectic acid, which is soluble in pure water, though insoluble in water containing strong acids or salts. As soon as the liquid ceased to give a precipitate with nitrate of silver, the mass was taken from the filter, pressed between folds of blotting-paper, in order to take up the alcohol, and then treated with boiling water for some time. A milky liquid was thus obtained, which was set aside for some time in order to allow the flocculent matter suspended in it, which prevented it from filtering readily, to settle. The liquid, having been decanted from the deposit, was filtered and evaporated, when it left an amorphous light brown residue, resembling gum or gelatine, and having the properties and composition of parapectic acid. The flocculent deposit consisted of pectic acid; but it was contaminated with a considerable quantity of colouring matter, from which it could, in most cases, not be separated without undergoing a change. If, for instance, it was dissolved again in caustic soda, and the process just described was repeated, it was usually converted for the most part into a substance soluble in waterthat is, into parapectic acid.

The second method of preparing the acid is far less tedious, and yields a product much freer from colour than the one just described. It differs, however, from the latter in one particular only, viz., in the use of a bleaching agent instead of caustic soda as a precipitant. To the watery solution of impure pectate and parapectate of soda, obtained in the same manner as before, there was added a clear solution of chloride of lime, which produced an abundant precipitate consisting mostly of pectate and parapectate of lime. By adding an excess of the bleaching solution, the colour of the precipitate, which was at first brown, became gradually lighter. As soon as it had lost all its colour, or retained only a yellowish tinge, it was filtered off, washed with water, and treated with dilute hydrochloric acid. The white flocks left undissolved by the acid were filtered off, washed at first with water and then with alcohol, and lastly treated as before with boiling water, which left the pectic acid undissolved. The filtered liquid left, on evaporation, a residue of parapectic acid, having only a faint yellowish tinge like that of the purest gum. It did not differ in composition from that prepared by the process first described, proving that the chloride of lime produced no decomposing effect, but merely

served to destroy and remove the colouring matter.

The following is a short account of the properties and composition of the various substances the preparation of which has been just described:

Cotton-Wax.

There can be no doubt that this substance must be classed with the waxes. bodies which are distinguished by their insolubility in water and alkaline liquids, their sparing solubility in alcohol and ether, and their high meltingpoint. Indeed it so closely resembles in many respects the better known vegetable waxes, such as the cerosine prepared by Avequin from the leaves of the sugar-cane, and the wax from the leaves of the Carnauba palm (Corypha cerifera), examined by Brande* and Lewy†, that its identity with one of these may be suspected. It has the following properties:—

It is insoluble in water, but soluble in alcohol and ether. If a concentrated solution in boiling alcohol be allowed to cool, the greatest part of the substance is deposited, causing the liquid to assume the appearance of a thick white jelly, like starch-paste, which, when examined under the microscope, is found to consist of minute scales and needles suspended in the alcoholic liquid. When the mass is filtered off and dried, it shrinks very much, and is converted into a coherent cake, which has a waxy lustre, is translucent, friable, and lighter than water, and does not soften when kneaded between the fingers. A specimen of the substance from East Indian cotton, when heated in the usual manner in a capillary tube, was found to melt at 86° C. to a transparent liquid, which solidified again at 81° C. Another specimen, from American cotton, fused at 86°, and became solid again at 82° C. According to Avequin, cerosine fuses at 82° and solidifies at 80°. Carnauba wax, according to Lewy, melts at 83.5. When heated on platinum foil, cotton-wax gives off an odour resembling that of burning fat, and then burns with a bright flame, without leaving any ash. If heated in a tube, it melts, emits a penetrating odour, and then volatilises completely, yielding an oily sublimate, which soon becomes solid and crystalline and seems to consist of unchanged substance. Singular to say, cotton-wax, when pure, is quite insoluble in caustic alkalies; and it is therefore difficult to account for its presence among the products extracted from cotton by soda-lye, unless it be assumed that it exists originally, not within the fibre, but on its surface, and is merely fused and mechanically detached by the action of the hot liquid. When treated with boiling dilute caustic soda-lye, it melts without dissolving, and the filtered liquid gives only a trifling precipitate with acid; but when carefully heated with hydrate of soda, it yields a compound which is entirely soluble in water; and the solution now gives, with acid, a copious white flocculent precipitate, which consists of a true fatty acid, formed by a process similar to that of ordinary saponification, or more so perhaps to that by which alcohols are converted into the corresponding acids. When cotton-wax is treated with fuming nitric acid, it does not dissolve, even when the acid is boiled for some time; it merely melts, and solidifies on cooling. But a change has, nevertheless, taken place; for if the excess of acid be poured off, and the undissolved fatty matter, after being washed, be treated with boiling caustic soda-lye, it dissolves entirely, and the solution gives, with acid, a white flocculent precipitate. By the action of nitric acid, therefore, the substance is probably transformed in the same manner as by the action of dry caustic soda.

In order to prepare the substance for analysis, it was kept in a state of

Philosophical Transactions for 1811, p. 261.

⁺ Journ. f. Prakt. Chemie, B. xxxvi.. S. 65.

fusion in the water-bath for several hours, then reduced to powder and placed in a bell over sulphuric acid. Its analysis yielded numbers corresponding in too parts to—

			I.	II.	III.
C	 		80.32	80.29	80.38
H	 		14.35	14.53	14.21
O	 	• •	5.30	5.48	2.11
			100,00	100.00	100,00

It would have been easy to devise a formula corresponding to these numbers; but as the quantity of material at Dr. Schunck's disposal was not sufficient to enable him to make any experiments to determine the atomic weight of the substance, the accuracy of any such formula would have been a mere matter of probability. That its composition is very similar to that of other vegetable waxes will be seen by comparing the above numbers with those obtained by Dumas* in the analysis of cerosine, and by Lewy† in that of Carnauba wax, which were as follows:—

		-	Cerosine.	Ca	rnauba W	ax.
C	 	 	81.00	 	80.36	
H	 	 	14.19	 	13.07	
0	 	 	4.84	 	6.57	
			100.00		100.00	

Its composition differs also but little from that of the wax-like body derived from the Ceroxylon andicola.

For the purpose of examining the product of decomposition which is obtained from cotton-wax by the action of dry caustic alkalies, Dr. Schunck took some of the substance, added caustic soda-lye, evaporated to dryness, and heated the dry residue rather strongly, then added water and evaporated again, repeating the process several times, until the product was found to be entirely soluble in water. An excess of acid was then added; the matter left undissolved was filtered off, washed with water, and dissolved in a little boiling alcohol. The solution on cooling deposited white crystalline flocks, which, after being filtered off and dried, had the appearance of a white opaque mass resembling stearic acid. This mass, when examined under the microscope, was found to consist of minute star-shaped aggregates of needles. When heated it was easily volatilised, yielding an oily sublimate which became crystalline on cooling. It dissolved easily in alkaline liquids, and the solutions frothed on being boiled. The solution in ammonia gave, with chloride of calcium, a white curdy precipitate. In boiling water it melted, forming transparent oily drops, which became solid and crystalline on cooling. In a capillary tube, it fused at 85° C. and solidified at 77° C. The quantity of substance was just sufficient for one analysis.

In 100 parts it contained -

79.86	٠	٠	٠		۰			 ٠	C
14'04	٠			٠			٠	٠	Н.,
6.10						۰	۰		0
100.00									

[†] Annales de Chim. et de Phys., t. lxxv., p. 223 [‡] Journ. f. Prakt, Chemie, B. xxxvi., S. 74.

The composition of this substance does not differ very widely from that of cerosic acid, the acid formed by the action of dry potash and lime on cerosine, which, according to Lewy, consists of—

C	 	 	 80.11
H	 	 	 13.55
0	 	 	 6.34
			100,00

There can be little doubt that cotton-wax is identical with the "resin" which, according to Persoz and others, is peculiar to cotton, and which is said to protect the filaments from the action of external agents. Dr. Schunck inclines to the belief that it is formed on the exterior of the fibres, and clothes them with a thin waxy covering (like the coating of a similar material sometimes found on leaves and fruit), and thus imparts to them their well-known property of resisting water. If it be supposed to be contained solely in the interior of the cells forming the fibres of cotton, it is difficult to conceive by what means any portion of it comes to be dissolved in the alkaline lye, in which, when pure, it is quite insoluble. Its solubility in alkalies is not promoted in any appreciable degree by admixture with the colouring matters of cotton; for on adding to it a quantity of either of the two colouring matters, and acting on the mixture with alkali, the colouring matter is simply dissolved, leaving the wax behind.

The quantity of cotton-wax obtained in the experiments was exceedingly small. It amounted to about 1 per cent of the weight of the brown precipitate thrown down by acid from the alkaline extract. It is by no means certain, however, that this was the total quantity contained in the cotton.

Fatty Acid from Cotton.

This substance, when prepared in the manner above described, has the appearance of a white mass consisting of microscopic needles arranged in spheres. It fuses at 55.5° C., and solidifies again at 50.5° C. When heated on platinum it melts, and then burns with a highly luminous flame. Heated in a tube, it is volatilised, leaving hardly any residue and furnishing an oily sublimate which soon becomes solid. It dissolves readily in alcohol and ether. The alcoholic solution reddens litmus paper slightly. It dissolves in warm caustic potash and soda-lye, as well as in liquid ammonia; and the solutions froth on being boiled. The solution in potash yields, on cooling and standing, a quantity of crystalline needles, while the solution in soda gives immediately a thick soap which fills the whole liquid. The solution in ammonia deposits, on cooling, shining crystalline scales. The compound with soda is obtained in a state of purity by adding carbonate of soda to the alcoholic solution of the acid, evaporating to dryness, treating the residue with boiling absolute alcohol, filtering, and evaporating. When this compound is dissolved in boiling water, and the solution is allowed to cool, it is deposited again as a gelatinous mass, which, when examined under the microscope, is found to consist of small needles, arranged in star-shaped or fan-shaped masses. The watery solution gives with the chlorides of barium and calcium white flocculent precipitates, with acetate of lead an abundant white precipitate, and with nitrate of silver a white flocculent precipitate which becomes only slightly discoloured on exposure to light or on heating the liquid. The alcoholic solution of the acid gives, with acetate of baryta, a white granular precipitate, which is soluble, though with difficulty, in boiling alcohol. With acetate of magnesia it gives at first no precipitate; but after some time a white crystalline deposit is formed, consisting of the magnesia compound. These reactions belong to the group of fatty acids of which stearic and palmitic acids are members. In order to ascertain the exact place in the series occupied by the acid_from cotton, it_was submitted to analysis, the following being the results obtained:—

		Calculation.		I.	· II.
C ₃₄	 	 204	75.22	75.27	75'45
H_{34}	 	 34	12.29	15.01	13.51
04	 	 32	11.86	11.83	11.34
		270	100.00	100.00	100.00

The formula $C_{34}H_{34}O_4$ belongs to margaric acid, one of the products derived from ordinary fats. Modern researches have rendered it almost certain that what was formerly called margaric acid is in fact a mixture of stearic and palmitic acids. In consequence, however, of the minute quantity of the substance obtained from cotton, Dr. Schunck was unable to undertake any experiments for the purpose of separating its constituents from one another, but was obliged to content himself with proving the presence of one of the ordinary products of the saponification of fats and oils among the bodies extracted from cotton by alkalies. The quantity procured from American cotton was, indeed, so small that he was hardly able to purify it sufficiently for the purposes of analysis, and the amount of hydrogen which it was found to contain differed accordingly rather widely from that demanded by theory; the presence of some impurity or other in this specimen was also indicated by its rather lower melting-point.

As regards this fatty acid, the question will naturally arise, whether it is to be considered a natural constituent of the fibre, or whether it is a foreign body introduced subsequently to the gathering of the cotton, either before or during the process of manufacture; but this is a question to which it is not easy to give a satisfactory reply. Persons practically conversant with cotton spinning say that it is impossible for the cotton to be contaminated with any substance of a fatty nature during the process of its conversion into yarn, provided ordinary care be taken, since it can only in consequence of gross carelessness come into contact with the oil or fat used in greasing the machinery. On the other hand, it is quite possible that after the cotton has been gathered, especially during the process of ginning, a portion of the oil of the seed may escape, diffuse itself among the fibres, and give rise to the formation of fatty acid in consequence of the action on it of the alkali. Dr. Schunck has not, however, failed in any of his experiments, whether made with East-Indian or American cotton, to obtain a small quantity of a solid crystalline fatty acid.

Colouring Matter A.

This substance is easily soluble in alcohol and is left on evaporating the solution as a dark brown, shining, brittle, amorphous resin, which is transparent in thin layers. In boiling water it softens and melts to a pasty mass, which

becomes hard and brittle again on cooling. It is insoluble in ether, and is accordingly precipitated on the addition of ether to the alcoholic solution. When heated on platinum it melts, swells up considerably, and burns with a bright, but smokeless flame, leaving a very voluminous coal, which gradually burns away, only a slight trace of ash being left. It contains nitrogen, and when heated with soda-lime gives off ammonia in abundance. It dissolves in concentrated sulphuric acid and in glacial acetic acid, giving dark brown solutions, from which it is re-precipitated by water in brown flocks. It is easily decomposed by boiling nitric acid, yielding a yellow solution, which on evaporation leaves an abundance of oxalic acid, but no picric acid. It is easily soluble in caustic and carbonated alkalies, giving dark yellowish-brown solutions, from which it is re-precipitated by acids in light brown flocks. The ammoniacal solution leaves, on evaporation, a dark brown amorphous residue, which does not dissolve again entirely in water, in consequence of a loss of a part of its ammonia during evaporation. The ammoniacal solution gives brown precipitates with the chlorides of barium and calcium, but none with sulphate of magnesia. With nitrate of silver it yields a dark reddishbrown precipitate, which dissolves completely in an excess of ammonia, giving a yellowish-brown solution, which remains unchanged on being boiled. The alcoholic solution of the substance gives brown precipitates with the acetates of baryta, lead, and copper. On the addition of an alcoholic solution of potash it gives a brown precipitate, which sinks rapidly, forming a glutinous deposit. A similar effect takes place when an alcoholic solution of soda is employed. The substance is easily soluble in a boiling solution of acetate of soda, and is re-precipitated by acids in brown flocks. When the substance in a finely divided state, as obtained by precipitation from its alkaline solution with acid, is exposed for some time to the action of chlorine, its colour changes gradually from brown to pale yellow. After being filtered off and washed with water, the product of the action dissolves easily in alcohol, and is left on evaporation as a brown transparent resin, which contains chlorine, but in other respects closely resembles the original substance.

The analysis of this colouring matter led to results corresponding in 100 parts to—

		1.	II.	HII.	IV.
C	 	 58.27	28.11	58.36	58.48
H	 	 6.43	6.40	5.00	5.80
N	 	 8.03		5.22	2.31
0	 	 27.28		30.2	30.41
		100.00		100.00	100.00

It will be seen that the composition of the substance varied, especially as regards the nitrogen, much more than it ought to have done, supposing it to have been perfectly pure. In consequence of the amorphous nature of the product, it is difficult to determine whether Indian and American cotton contain two distinct colouring matters, both easily soluble in alcohol and having the same general physical properties, or whether in one or both cases the specimens submitted to analysis, though essentially the same substance, were not chemically pure. It is difficult to obtain, in a state of purity, an uncrystallisable resinous body having few characteristic properties; and the results arrived at by examining the composition of such bodies are seldom satisfactory.

Colouring Matter B.

This substance is deposited from its solution in boiling alcohol as a brown powder, which, after being filtered off and dried, forms coherent masses of a colour varying from light to dark brown, which may be easily broken, the fracture being dull and earthy. In boiling water it softens and yields a dark brown cake. It is almost insoluble in cold alcohol, and when it has once been dried it dissolves with great difficulty even in boiling alcohol. By this property it may easily be distinguished from the other colouring matter, which it closely resembles in most other respects. When heated on platinum, it burns without previously melting; and the carbonaceous residue burns away with difficulty, leaving at last a bulky white or yellowish ash. This ash is not alkaline, and consists principally of alumina and sulphate of lime. The ash was in most cases so considerable that Dr. Schunck was led to suspect that this colouring matter might possibly be a compound of the other with some earthy base, in which case the striking similarity in the properties and reactions of the two substances would have admitted of an easy explanation. In order to submit this supposition to the test of experiment, he took some of the colouring matter B, pounded it very fine, added a little concentrated sulphuric acid and then absolute alcohol, after which the whole was well stirred in a mortar and left to stand for some time. The liquid, which had a brown colour, was filtered and mixed with water, which gave a brown precipitate. This was filtered off, washed with water, and dissolved in boiling alcohol. The solution left, on evaporation, a brown resinous residue, which was almost insoluble in cold alcohol, and contained, therefore, none of the colouring matter A.

In determining the composition of this substance, results were obtained which, after deducting the ash, correspond in 100 parts to—

			I.	11.	III.	IV.	V.	Mean.
C	٠.		 57.28	57.53	57.32	58.47	58.26	57.77
H		٠.	 6.25	6.26	6.33	5.77	5.65	6.02
N	٠.		 9'39	9.29	9.23	7.77	7:+3	8.74
()			 27.08	26.62	26.83	27.99	28.66	27.44
						-	allered and the second	
			100,00	100.00	100.00	100.00	100.00	

It will be seen that in this case, as in that of colouring matter A, there is a wider discrepancy in the numbers yielded by analysis than ever takes place with a perfectly pure substance. Nevertheless the composition of colouring matter B, as represented by the mean of the numbers just given, approaches so closely that of colouring matter A from East-Indian cotton as to make it probable that, when pure, the two bodies do not differ in composition from one another.*

From what has just been stated it may be inferred that, as regards their chemical properties, these colouring matters possess very little interest. It is simply the fact of their being the cause of the yellow or brownish tinge natural to raw cotton which gives them any importance, and makes a

Fig. 18 It is quite possible that these colouring matters may be products of decomposition derived from some other substance existing in the fibre, and that they may consequently vary in composition according to the strength of the solvent used for extraction, the time during which it acts, and other circumstances.

knowledge of their properties desirable from a practical point of view. The darker shade of colour seen in the so-called "nankin" cotton is probably due to a great excess of these colouring matters existing in the fibre. It is certainly not caused by oxide of iron, since the ash of this kind of cotton contains no more iron than that of ordinary kinds, and the colour is for the most part removed by treatment with caustic alkali.

Pectic Acid.

A considerable portion of the organic matter extracted from cotton by caustic alkali consists of a body belonging to the pectine class. Which member of this class it is that exists originally in the fibre is a question on which no opinion is expressed, though there can be no doubt that the precipitate produced by acid in the alkaline extract of cotton contains pectic acid itself. This acid, which is insoluble in water, is almost entirely converted during the process of purification adopted into an acid soluble in water, which seems to be identical with Frémy's parapectic acid. The chief properties of this soluble acid are as follows:—

On evaporation it is left as a light yellow, amorphous, translucent substance resembling gum or gelatine. When heated on platinum it burns with a slight flame, without previously melting, leaving a little ash, which is yellow or brown and only slightly alkaline, and consists chiefly of alumina, together with oxide of iron and lime. The watery solution is clear and colourless and reddens litmus-paper. It gives abundant white flocculent precipitates with sulphuric, nitric, hydrochloric, and acetic acids, as well as with baryta water and acetate of lead. When the watery solution is mixed with several times its volume of alcohol the liquid gelatinises, the jelly being perfectly clear and transparent. The substance is decomposed with difficulty by boiling nitric acid; and no oxalic acid can be discovered among the products of decomposition. When treated with strong caustic potash or soda-lye it turns yellow; and on boiling, the liquid assumes a bright yellow colour similar to that of chromate of potash solution. On continuing the action of the caustic alkali the substance is gradually dissolved; but on adding an excess of acid no precipitate is produced, showing that a complete change has taken place. In very dilute potash or soda-lye, as well as in liquid ammonia, it dissolves readily on boiling. The solutions when mixed with alcohol give colourless jellies, consisting of the salts of the respective bases. If the precipitated ammonia compound, after being filtered off and washed with alcohol until the excess of ammonia is removed, be treated with boiling water, it dissolves, and the solution leaves, on evaporation, a transparent, amorphous, nearly colourless residue, which separates from the sides of the vessel in shining scales. This residue dissolves again entirely in water. The solution is neutral to testpaper, and gives flocculent precipitates with alkaline salts, such as chloride of sodium and chloride of ammonium, as well as with all earthy and metallic salts which were tried, except perchloride of mercury and chloride of gold. The precipitate with nitrate of silver, which is white, does not change much when exposed for several days to light, and when dissolved in ammonia yields a solution which on being boiled becomes yellow but deposits no metallic silver. When a solution of the acid in a sealed tube is heated for some time in the water-bath it is found to have undergone a complete change. The

liquid leaves, on evaporation, a brown, slightly deliquescent residue, which dissolves again with ease in cold water. The solution has a strong acid reaction. With caustic alkalies it strikes a deep yellow colour. It gives flocculent precipitates with baryta-water and acetate of lead, but none with hydrochloric acid or chloride of sodium. With nitrate of silver it gives a precipitate which blackens on exposure to light, and when made alkaline it reduces oxide of copper at the boiling-heat. The acid has, in fact, been converted into the substance, or mixture of substances, to which Frémy has given the name of metapectic acid.

The reactions just described are of themselves almost sufficient to prove that the acid obtained from cotton is one of the derivatives of pectine. All uncertainty on this point, however, was removed by an examination of its composition, which, if the ash be deducted and the small amount of nitrogen, which evidently belonged to some slight impurity, be neglected, led to the following numbers:—

			I.	II.	III.
C	 	 	40.01	39.98	39.82
H	 	 	4.81	4.75	4.88
O	 	 	54.58	55.27	55.30
			100.00	100,00	100.00

The results arrived at by different chemists in examining the composition of pectine and its derivatives vary so much that it is difficult to identify any member of the class by means of analysis only. The composition just given approaches that of Frémy's parapectic acid, which, according to him, consists of

It has been already mentioned that the acid originally contained in the alkaline extract of cotton is insoluble in water, but is gradually converted during the process of purification into a soluble acid. Of the insoluble acid, the true pectic acid, a sufficient quantity for the purposes of analysis was obtained on only one occasion. It was left undissolved by boiling water in the preparation of the specimen of soluble acid employed for the second of the above analyses, and when dry was dark grey and horn-like, and was with difficulty reduced to powder.

After deducting the ash, it gave numbers corresponding in 100 parts to-

According to Chodnew,* pectic acid contains in 100 parts-

Frémy's experiments led him to infer that there exists in plants a body insoluble in water, which he calls pectose, and which, by the action of acids,

^{*} Annalen d. Chem. u. Pharm., B. li., S. 363.

alkalies, or the pectic ferment (pectase), is converted first into pectine, then into pectic acid, and other products in succession. It is not improbable that this may be the case with cotton fibre also; but as yet no experiments have been made to decide this point.

Pectic, parapectic, and metapectic acids have recently been discovered by Divers and Abel among the products of the spontaneous decomposition of gun-cotton; and the latter maintains that "these substances have been so frequently obtained, that they must be regarded as general products of the gradual decomposition of gun-cotton." If from this we are to infer that the acids named are derived from nitro-cellulose itself, Dr. Schunck thinks it will be granted that there is little probability in the supposition, and that it is safer to assume that these acids pre-existed in the cotton fibre, in the form of pectine or pectic acid, before the action of nitro-sulphuric acid on it.

According to Frémy, the pectic acid of plants is always accompanied by a small quantity of an albuminous substance. It seemed not improbable that this might also be the case with the pectic acid of cotton; but as the preparation in a state of purity of a body of this class when occurring along with the other constituents of cotton fibre would without doubt have been a very difficult task, it was determined to ascertain whether, by the action of caustic alkalies on the impure pectic acid of cotton, any of the products of decomposition of albumen could be procured, some of which are bodies of very characteristic properties. For this purpose a quantity of the brown precipitate thrown down by acid from an alkaline extract of cotton was exhausted as far as possible with boiling alcohol; it was then dried, a quantity of hydrate of soda, equal in weight to that of the dry residue, together with a little water added, and the mixture heated over the fire in an iron ladle, with the precautions which are usually observed in the preparation of leucine and tyrosine from animal matters. The decomposition was accompanied by a copious evolution of gas and a strong smell of ammonia, the latter being probably derived for the most part from the colouring matter present, which had not been completely removed by the alcohol. The disengagement of gas having ceased, the mass was treated with boiling water, in which it dissolved almost entirely, yielding a dark brown solution. To this there was added an excess of acetic acid, which gave a brown flocculent precipitate. This having been filtered off, the liquid was evaporated. During evaporation it deposited a considerable quantity of a brownish-white crystalline powder, consisting of oxalate of soda. This was filtered off, purified by re-crystallisation from boiling water, and converted into oxalate of lead, from which there was obtained, in the usual manner, a quantity of pure crystallised oxalic acid, weighing 18:3 grms. The mother-liquor of the oxalate of soda was evaporated. It left a dark brown syrup, which was dissolved in boiling alcohol, and mixed with concentrated sulphuric acid as long as any sulphate of soda was precipitated. The latter having been filtered off, acetate of lead was added, and the liquid, after being filtered from the precipitated sulphate of lead, was deprived of its excess of lead by means of sulphuretted hydrogen, filtered again, and evaporated. The brown syrup which remained was mixed with a large quantity of alcohol and left to stand for several weeks. During this period the liquid gradually deposited a quantity of white crystalline needles, which, after being filtered off, washed, and dried, weighed o'6 grm. These crystals possessed the properties of tyrosine, and were quite free from leucine. Now as tyrosine is only formed, as far as we know, from albumen and bodies of the same class, it is almost certain that cotton contains a small quantity of an albuminous substance. The oxalic acid obtained in this experiment was doubtless derived from the pectic acid. Of the ratio in which the latter stands to the albuminous matter, some estimate may be formed by that subsisting between their respective products of decomposition.

The precipitate produced by acid in an alkaline extract of cotton contains, then, the following organic substances:—

- r. Cotton wax.
- 2. Margaric acid.
- 3. A colouring matter easily soluble in alcohol.
- 4. A colouring matter sparingly soluble in alcohol.
- 5. Pectic acid.
- 6. Albuminous matter.

Of these various bodies the pectic acid far exceeds the others in quantity. Then follow the colouring matters. The three other constituents are present in extremely minutes quantities only. Dr. Schunck thinks it possible that cotton fibre may contain, besides these, other organic substances which are soluble in water or alkali, but are not afterwards precipitated by acid. It is well known that cotton, during the process of bleaching, loses about 5 per cent of its weight, whereas the total weight of all the substances obtained in Schunck's experiments amounts to hardly \(\frac{1}{2}\) per cent. It is, however, not improbable that a portion of the matter which escaped observation may consist in great part of parapectic acid. This body, though insoluble in tolerably strong acids or saline solutions, is soluble in pure water. When, therefore, it is precipitated from an alkaline solution, the precipitate, on being filtered off and washed, begins gradually to dissolve as soon as the greatest part of the precipitant has been removed. This was observed on washing the precipitate thrown down by acid from the alkaline extract of cotton. When the acid has to some extent been removed, the wash-water begins to becomes thick and slimy, and runs through very slowly, in consequence of its dissolving a portion of the parapectic acid of the precipitate. A part also of the pectic acid originally present may undergo a further change by the action of the alkali, and be converted into the metapectic acid of Frémy, which is very soluble in water, and is not precipitated by stronger acids. The loss of weight sustained by cotton during its treatment with alkali, and not accounted for by Schunck's experiments, may therefore be due to such derivatives of pectine as are not precipitated by acid, or are subsequently removed by washing the precipitate with water.

CHAPTER IV.

BLEACHING.

BEFORE either spun cotton yarn or woven tissue are fit for dyeing or printing, they undergo a series of mechanical and chemical processes to free them from all adhering substances, such substances either naturally belonging to the fibre or being purposely introduced during the operations of spinning and weaving. Pure cotton is of a dirty yellow colour, which if not removed by bleaching would materially affect and change the brighter shades of dyes imparted to tissues; moreover, the effect of many beautiful printed patterns is due to the brilliant white ground upon which they appear. Bleaching also removes from cotton all grease, which if allowed to remain would prove very injurious both in dyeing and printing, either preventing the fixation of colour, or else acting as a mordant, especially after partial oxidisation by the air, and thus attracting the dye in an irregular manner.

Before bleaching, the cotton fabric is singed, in order to remove the nap and render the surface perfectly smooth. This is done either by passing the fabric through a gas flame or over a heated copper plate. In the latter case there was formerly great waste of fuel in maintaining the heat of the plate owing to its free radiation into the atmosphere, but this has been remedied by an invention of Mr. Thom. This consists of enclosing the plate in a brick arch so that no air can enter the chamber except that passing in with the stuff, and the limited quantity thus admitted is conducted by flues into the furnace which heats the plate. Messrs. Joshua Schofield and Sons have introduced a new gas singeing machine, patented by Mr. James Cook. Instead of the fabric being drawn through the flame as in the old method, the flame is made to flow upon the surface of the fabric, the nap being thereby removed without destroying the fibres. The flame employed in this method is a mixture of coal-gas and oxygen, the heat of which is so great that the fabric can be passed over it with such rapidity as to remove the nap without injuring the fibre. The machine is both quick and economical, and like Mr. Thom's, does not allow of the escape of any offensive odour during the operation. At the works of Messrs. Edmund Potter and Co. more than 4000 pieces of calico were singed in a day with a consumption of only 1000 cubic feet of gas per 1000 pieces.

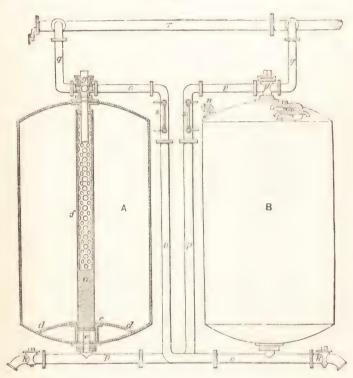
The following substances adhere to and become mixed up with the cotton:-1st, a brown-coloured incrustating substance insoluble in water and alkaline solutions, but capable of becoming soluble in water under the joint influence of air, damp, and sunlight, or by the action of chlorine and hypochlorous acid; 2nd, according to M. Penot, a resinous substance soluble in alkaline lyes; but the quantity of both these substances found in cotton is small.

The following substances are also imparted to cotton fabrics by the operations of spinning and weaving:-Ist, starch and paste; 2nd, fatty matters; 3rd, a soap of copper (due to the action of the fatty substances upon the copper teeth of the comb); and 4th, of dirt from the hands of the operatives. It is impossible to act upon the incrustating matters until after the removal of the last-named impurities, for which purpose alkaline lyes are resorted to. These, besides eliminating grease and dirt, promote the removal of incrustating matters by predisposing them to oxidisation. Cotton is easier to bleach than any other fibre, because it contains but few impurities and consists mainly of cellulose, which resists uninjured the action of pretty strong chemicals, so that energetic agents may be safely employed. Wool and silk cannot be so actively treated. The theory of bleaching is that the greasy matters are removed by caustic or carbonated alkaline lyes, while the incrustating substances are destroyed by an oxidating process; its practice consists of the following operations: -- "Singeing," "rot steep" or "wetting-out steep," "liming," passing through a solution of chloride of lime, "bowking," passing through weak acids, chiefly hydrochloric acid, washing, squeezing, and dyeing. The "rot steep," so called because the flour or size with which the goods were impregnated was formerly allowed to ferment and putrefy, is intended to thoroughly wet the cloth. This takes some time, as the fabric, on account of the greasy matters contained in it, throws off the water in places, and if it be not thoroughly wetted there is risk of irregularity in the after processes. "Liming" takes place in large kiers or kettles capable of holding from 500 to 1500 pieces of cloth. The lime is carefully slaked some days previous to use, and sifted to prevent the introduction of small lumps of quick-lime into the kiers into which it is equally distributed: the stuff is then pressed down into the kiers, and the boiling commenced and continued for a period of from twelve to sixteen hours. After this the liquor is drawn off and clear water run in to cool the pieces, which are then taken out and washed. Liming usually takes place at low pressure, but a patent process, which employs a pressure of upwards of 40 lbs., appears to answer very well and saves time. It is very important that the goods remain entirely covered with liquid during this operation, since, according to Dr. E. Schwartz, the action of lime upon cloth is highly destructive if it be at the same time exposed to the air. The latest of the methods of bleaching under pressure is that of Mr. Barlow. Of this method and the machinery employed we give illustrations. In that of Mr. Barlow's, Fig. 1 is an elevation showing a pair of kiers, fitted with distributers, &c. A and B are the kiers (which it is preferable to make of strong boiler-plate iron), the kier A being shown in section, and exhibiting the distributors, &c.

At the bottom of the kier is a plate of an umbrella shape, c. This plate spreads over about three-fourths of the bottom of the kier; it is perforated with holes all around its outer ridge, at d, which rests upon the bottom of the kier; all the rest of the plate being solid. This plate is fastened in the centre to an iron block, e, which stands upon the bottom of the kier, in the centre, over the outlet hole. The block e is pigeon-holed at the bottom, so as to allow the liquor to pass from the kier. A socket is left in the upper part of the block e, to admit the insertion of the distributor, f. This distributor is made of dimensions corresponding to the size of the kier; it is solid for some distance from the bottom, and above that is hollow and perforated as full as

possible with holes until within a few inches of the top of the kier, where it is connected with the tap g (an ordinary two-way tap, which admits either steam or liquor, or shuts off both) by an inlet pipe, which dips for some distance inside the distributor. o o is the pipe connecting the top of the kier a with the bottom of kier a, and b b is the pipe which connects the top of kier a with the top of kier a; a are steam-pipes from the main-pipe, a; a is the manway, through which the goods are introduced and removed; a the pipe and tap, through which the working liquor enters the kier; a are gauges, by which it is seen when the liquor has passed from one kier and has entered the

Fig. 1.



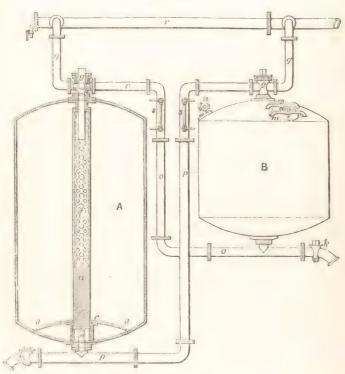
other; kk are draw-off taps connected with the pipes o and p, by which the kiers can be emptied of spent liquor, water, &c.

In operating with this apparatus, the goods are introduced through the manways, laying them at the bottom, upon the umbrella plate and the bottom of the kier; the kiers are filled to the top, and the manways closed. Steam (a high pressure preferable) is then admitted, through the two-way taps, g g, from the pipes q q into the kiers; the steam forces all the cold water, air, &c., out of the goods (being very much assisted in its action by the distributor) through the perforated edge of the umbrella plate, at d d, the holes

in the block e, and out of the kier by the taps k k; the taps are then closed. The boiling bowking liquor is next run in, by tap n, to kier B, and steam again admitted, which forces the liquor through the goods out of the kier B, up the pipe o o, and into kier A, its tap, g, being turned to admit the liquor. When all the liquor has passed into kier A, steam is shut off from kier B, turned on to kier A, and, in like manner, forces the liquor through the goods in kier A, up the pipe p p, and into the kier B again. This is repeated until the goods are sufficiently worked.

By this system all the cold water, air, &c., is first expelled, by the highpressure steam, from the goods, which, then almost dry, and heated by the





steam, are in the best state for receiving benefit from the bowking liquor, which is admitted boiling, is forced through them, and followed up by the steam; and throughout the whole of the operation they are subjected alternately to the action of the steam and the liquor. By this alternate steaming and liquoring, the goods are much more thoroughly cleansed than has been the case in former kiers.

Fig. 2 is a modification of Fig. 1. The various parts of the kiers correspond with the description of Fig. 1; the principle and the mode of working are

precisely the same; the only difference is, that kier B is reduced in size to about one-third that of kier A; it is not charged with goods, and is only intended to receive the liquor when forced through the goods in kier A. The liquor is boiled in kier B by a modified distributor, and is forced from it into kier A, and this is repeated until the goods in kier A are sufficiently worked.

This modification is only recommended where small quantities are done, and the kiers required would be too small for working in conveniently. Where quantities above 300 pieces, or say 1,500 lbs. of goods a day are done, it will be very much better to adopt the double kiers, as in Fig. 1; for they take up very little more room, require only the same attendance, and, with the exception of a few feet of piping, they need only the same pipes, taps, gauges, and other fittings, so are not much more expensive to put up than this, Fig. 2, while double the quantity can be done in them in the same time, for both kiers can be crammed with goods to the very top.

Even when there are only sufficient goods to fill one kier it is better to divide them, putting half into each kier, as the liquor is kept hotter, and there is less condensation of steam in working, than when the liquor is forced from the

kier charged with goods into an empty one.

Mr. Kent, of Moscow, Russia, and of Nottingham, has patented an improvement in cleansing and bleaching, much used by cleaners working on a small scale. The improvement consists in subjecting the cotton-yarn or fabric to the following process:-Lime and soda are mixed (in the proportion of about 2 lbs. of carbonate of soda to 1 lb. of lime) with water, and allowed to stand to settle, when the clear liquor is drawn off or separated from the solid matters. It is found that the strength of the liquor when used should mark about 11 degrees of Twaddle's hydrometer. A strength of 11 degrees is found sufficient for fine light goods, and for heavier goods a greater strength is required. The yarn, thread, or fabric, or other preparation of vegetable fibres, is steeped in this liquor for from thirty to fifty minutes, more or less, as the case may require. Fine goods require about thirty minutes, and stouter ones a longer time in proportion. The process of cleaning and bleaching is then finished in the ordinary manner by washing, and then treating the fibrous materials with dilute sulphuric or hydrochloric acid and chloride of lime, but this part of the process requires less time, by reason of the fibrous materials not having been boiled for a great length of time with crude materials. A workman will readily judge of the effect produced, and he will find that it is not necessary to retain the yarns or fabrics in either of the liquors more than from forty to fifty minutes. By these means ordinary bleaching is accomplished in a few hours instead of occupying days. When the fabrics are to be dyed with madder in order to render them suitable to be so dyed, or as it is commonly called "madder bleached," the fabrics after being steeped and prepared as explained, are boiled for two or three hours in a weak solution of carbonate of soda and resin. The greasy matters are formed by the lime into a sort of insoluble soap easily removed by the after process.

"Souring" removes all excess of lime and breaks up the insoluble lime soap; it still leaves the grease upon the cloth, but in such an altered state as to be easily removable by the subsequent "bowking." Hydrochloric acid is sometimes employed in this souring, but very dilute vitriol may be used. The hydrochloric acid sours are used cold and at a strength of 3° Twaddle. The

bowking or boiling with alkali and soap dissolves and removes all grease and dirt from the cloth, leaving the cotton nearly pure. The alkali employed is soda-ash; the soap is that made from prepared resin, and having the specific effect of improving the whites during the subsequent process of dyeing. This boiling need not be so long as the liming, the time required, however, depending upon the size of the kier and the number of pieces. The last process, that of passing through a clear solution of bleaching-powder, destroys the slight buff or cream-coloured tinge still adhering to the cotton. The solution of bleaching-powder is so weak that an ordinary sized piece of calico does not probably take up more than a quarter of an ounce of the soluble matter contained in it. The goods are allowed to remain some time with the chloride of lime in them, and are finally passed through sours to complete the operation. The acid sets the chlorine free from the bleaching-powder, and completes the destruction of the colour, at the same time removing the lime and acting on any traces of iron that may be in the cloth. This souring should always be made with hydrochloric acid, as it obviates the danger of any sulphate of lime being fixed in the fibres or of giving bad whites in dyeing, effectually removes any iron, and leaves the goods softer. Tables of strengths and proportions of substances employed in bleaching are not of much value, since they must be modified according to circumstances, but as a kind of guide or example the following particulars may be quoted:-For 14,000 yards of ath printing cloth, 66-reed, 250 lbs. of quick-lime were used in the liming; 110 lbs. of hydrochloric acid for the first souring, and 140 lbs. of soda-ash at 48 per cent alkali, and 80 lbs. of prepared resin, or resin soap made with resin, and caustic alkali were used in the bowking. The last souring was sulphuric acid sour at 3° (37.4 F.) The quantity of bleaching-powder was not ascertained, but the solution stood at 1° = 1.006 sp. gr.

Chloride of lime is generally termed chemick in the dye-house, and the solutions are made up to half a degree Twaddle, or 1002'5, but in some establishments this is increased to 5°. There is the danger of rotting the cloth when very strong chemick is employed, the process generally consisting in passing the articles rapidly through with the calender in order to saturate them, and then to pass them through the acid bath, the final operation being the washing. The calender renders the passage through the chemick very rapid, so that strong solutions even for fine goods can be employed. The chemick must be clear, for any pieces or lumps of the chloride of lime coming into contact with the cloth would rot or burn it, as the term runs, leaving holes. The chloride of lime of commerce is a mixture of chloride of calcium and hypochlorite of lime. In the process of oxidising the foreign matters, which it is the purpose of bleaching to remove, the chloride is inefficacious, but the hypochlorite under the influence of the water or that of the carbonic acid of the air sets free oxygen, in its turn rendering the colouring matter soluble; the oxygen is separated according to the following equation:-

 $CaO,ClO = CaCl + O_2,$

that is, one atom of hypochlorite of lime sets free two atoms of oxygen; while one atom of free chlorine sets free only one atom of oxygen, according to the equation—

Cl + HO = HCl + O.

We thus see that the mixture known by the name of chloride of lime contains only one-half of its chlorine in effective condition. After the cloth has been

passed through the liquors employed in the process of bleaching it becomes necessary to discharge the fluid, and this operation is effected by squeezing rollers or squeezers. These are rollers generally worked under steam-power, the upper one being caused to bear upon the cloth by its own weight, or by means of a weighted lever. There are many varieties of these machines, the description of which belongs, however, to mechanical engineering, and is not an essential of the chemical processes of bleaching.

When squeezed, sometimes effected over rollers heated by steam, the cloth, if required for printing, needs no further operation, but if intended for the market it must be "finished," that is, starched and calendered. Many bleachers prefer to prepare their own starch from flour, as they thus avoid the drying process, for which the manufacturer of the starch must be paid. The starch is coloured with blue, generally ultramarine. It is disseminated over the cloth by means of rollers dipping into the starch, other rollers removing the excess. The starch need not be pure; fine clay or gypsum is sometimes employed as well. The pieces of cloth are occasionally artificially weighted with sulphate of baryta during the finishing, or with silicate of soda. The object of such an addition is to render the cloth solid in appearance. The calendering machine is really an ironing machine, surface and gloss being imparted to the cloth by means of heated rollers. The pieces when calendered and finished are subjected to hydraulic pressure.

Bleaching Muslins.

Muslins are bleached in the same manner as other cotton goods: Mr. Barlow employs solutions of the same strength, and does not consider that muslins need any special treatment. Only in cases where goods have coloured threads woven into them or colours printed on them must great caution be used; then it is desirable to employ weak solutions, repeating the operation often rather than allowing it to be continued for a length of time. It is possible to perform the entire bleaching in one operation, but then the goods would be made rotten: a certain strength of bleaching solution or soda leaves the fibre unattacked, while a more concentrated solution destroys the fibre as well as the colouring matters. It is often required to bleach the white ground of printed goods, where the ground has taken up sufficient colour to deteriorate the brilliancy of the white, and which soap would be powerless to remove. A solution of bleaching-powder at half a degree Twaddle is then employed. The liquor should be tested with a piece of Turkey-red dyed stuff; if too strong the colour will be discharged.

Muslins when finished and dried without motion become very hard, rigid, and rough to the touch; they are therefore stretched during drying, the lines of selvage being moved backward and forward so that the weft threads may rub against each other and not become united. This method of drying imparts the peculiar spring or elasticity to muslins.

Bleaching Cotton Stockings.

We shall from time to time in the progress of this work give descriptions in technical terms of processes which have been found advantageous for special purposes. These descriptions will differ from the rest of the work in being

didactic, the aim being to supply short practical recipes to be read at the side of the beck. We commence with a recipe for bleaching cotton stockings:—

too dozens of stockings are boiled for five to six hours in a lye made of 1 lbs. of caustic soda, after which they are to be rinsed in cold water. During this time dissolve 25 lbs. of good dry chloride of lime in warm water, and fill a barrel with it. Let the liquor settle, then transfer the clear liquid to a bleaching-tub of stone or wood. The latter cemented is the best and cheapest. The liquid should mark 1½° Baumé; but the glass test cannot be relied upon to ascertain the required strength, as the spindle might show ½ or 1° Baumé of other ingredients than the combinations of chlorine, such as carbonate of lime, &c. The strength of the liquor, is, however, very easily and simply ascertained by the experienced workman. The liquor ought to smell strongly of chlorine when held close to the nostrils; the goods should become considerably bleached after twenty-five minutes' immersion; but if they remain raw coloured more chloride of lime is required.

The boiled and rinsed stockings are now entered into the bleaching-vat and handled for a few minutes; then allowed to remain for six or more hours, perhaps over night. If the liquid is made a little warm, say 90° F., the stockings will bleach in two hours, and be ready to be taken out and rinsed. Then pass them into a vat filled with clean water to which 6 lbs. of sulphuric acid has been added. The strength of this sour water can be ascertained by the taste. The stockings ought to lie in this sour for about half an hour, when they are rinsed again in fresh water. Now they are ready to be scoured in the fulling-mill with warm water and white soap, enough of the latter to make a foam, after which they are rinsed and dried for the market.

If the stockings require blueing, then add I oz. of ultramarine to the soap in a tub large enough to hold about 25 dozens of stockings, or a mill full at a time. The ultramarine and soap must be stirred well; the stockings entered to get the blue even, and then fulled for about fifteen minutes or more; then taken out and carefully rinsed. As the ultramarine is not a dye, but only a fine powder, of course too much or uneven rinsing will injure the appearance of the fabric.

If the goods require stiffening, add ½ lb. of boiled starch to the soap while scouring. A very fine shade of blueing, and which is fast, is produced by passing the stockings, after they have been bleached, through a bath containing the solution of 1 lb. of blue vitriol and 2 ozs. of arsenic; after that, through the soap, as usual, and scoured.

Caustic soda at once makes soap of the oil or grease in the stockings during boiling, and is therefore superior to soda-ash. It is best made by the dyer himself as follows:—

Dissolve 25 lbs. of soda in a barrel filled with warm water, to which add 5 or 6 lbs. of slaked lime. Let the whole settle, and use the clear liquor, which is a solution of caustic soda. A too large quantity of lime is immaterial, as the soda will take up only a certain quantity to make it caustic. The settlings may be leached for future use.

Bleaching Cotton Stockings Merino Shade.

Have the stockings all bleached as described; then add to the soap in which the stockings are fulled 2 ozs. of turmeric to every mill full of hose.

Rinse and dry in the shade, because the colour is very fugitive. The bleached goods might also be coloured after scouring with fustic and alum; the colour would be more permanent, but the process would require a longer time. Hot bleaching makes the goods appear woolley, and so does a brushing machine when they are dry.

Bleaching Cotton Stockings with Turkey-Red Tops.

Boil roo dozens with 5 lbs. of soda and 4 lbs. of soap for several hours, then take them out and rinse. They should be now entered in the bleachingvat, which ought to be moderately strong. Handle the goods well, and let them lie in the liquor for a few hours, or until they are bleached enough; then take them out, allowing them to remain in the air as short time as possible. They should then be soured for half an hour, rinsed, and scoured with soap. Inferior Turkey-red dyed goods need great care in bleaching.

Bleaching Raw Cotton in Small Quantities.

If the same process were adopted as for stockings it would be tedious and expensive, but the bleaching of raw cotton on the small scale is easily effected by the following method:—

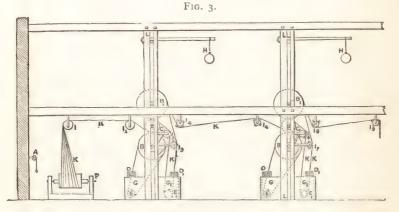
Boil the cotton in fresh water, without any lye or soda, only a few minutes, merely to saturate it. Long boiling would injure the fibre for spinning. Then pass the cotton into the bleaching-vat containing chloride of lime in such quantity as the operator may consider necessary. The cotton should be handled for fifteen minutes, then allowed to remain for four or five hours, afterwards being placed upon an inclined board to allow the liquor to drain back. The cotton is now rinsed in small quantities, and to every rinsing add I lb. of diluted sulphuric acid; stir the cotton in this sour for a few minutes, then let it off, and give the cotton a few more waters, so as to rinse all the acid away; then dry. The cotton will be quite white and easy to spin. The expense, inclusive of drying, will amount to about twopence per lb.

The Continuous Process of Bleaching.

By all dyers and bleachers having extensive business the continuous process, sometimes known as the "new," the "Bentley," or "Pendleton" process, is generally adopted, effecting a considerable economy in time and labour. The process was first patented by David Bentley, of Pendleton, in 1828, and in principle consists in drawing the goods successively through all the bleaching solutions, the pieces being made continuous with the aid of the sewing machine. The following is a general outline of the operations:-The pieces having been sewn together with the aid of a machine, are arranged in a carefully-constructed rope-like coil, being generally drawn through an aperture of smooth glass or earthenware to impart this form. When the pieces have been singed they are drawn into and boiled in the first kier, containing 1 lb. of caustic lime to 14 lbs. of cloth. The kier is constructed to hold about 500 gallons, and the boiling is continued for thirteen hours. The pieces are next washed in the washing machine, and are then passed through a sour of hydrochloric acid at 2° Twaddle. Supposing 3500 lbs. of cloth to be used, it is next bowked in a soda-ash and resin solution containing 170 lbs. of soda-ash to 30 lbs. of resin to 500 gallons of water. This boiling is

continued for sixteen hours, and the goods are again washed. The cloth is next saturated with chemick or a solution of chloride of lime for two hours, the density of the solution being about ½° Twaddle, when it is again washed. The continuous length is now boiled in a kier for five hours with 100 lbs. of crystals of carbonate of soda. After washing it is chemicked as before; then soured in hydrochloric acid of 2½° Twaddle. The cloth is next allowed to drain, is washed until quite clean, squeezed between rollers, finally being dried over steam cylinders or by means of a hydro-extractor. To effect these operations in one continuous process, many improvements have been suggested upon the plan pursued originally by Bentley, but as the principle is undoubtedly due to him, we shall describe the apparatus as it first appears in his patent.

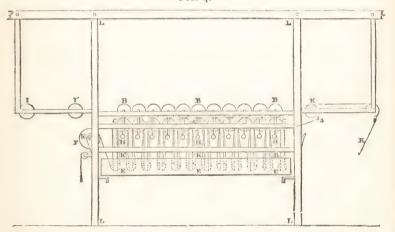
Fig. 3 is an end view of two calenders, each having two larger rollers, B and B¹, a smaller driving roller, c, two racks, D and D¹, placed upon two cisterns, G and G¹, inside of which are two rollers, E and E¹, having four square ribs upon each, to shake the goods as they pass through the cisterns.



At F is a series of rollers, upon which the batches of goods are placed. The calender cheeks are made fast at the feet, at the middle, and to the top of the building, having levers and weights, H, to give pressure to the calender bowls. Near the end walls of the building are two rollers, one of which is shown at A; upon each of these a soft cord is used as a guide for conducting the goods through the machinery and cisterns. The operation is commenced by passing one end of the cord through the rollers B and C, down to cistern G, under roller E, through the most remote division of rack D, and again through calender rollers at B and c, repeating the same, but observing to keep the cord tight, and to approach one division nearer in rack p each revolution until each division is occupied, when the end must pass over c, under and round B1, down to and over the guide-roller 13, through the nearest division of rack D1 into cistern G1, under roller E1, over guide-roller I2, and again over roller c, under and round B1. This course must be repeated, observing as before to keep the cord tight, and to receive one division of rack D1 every revolution, until each division of rack D1 is occupied, when the end must pass

over from B¹ under I⁴. The cord now forms a sort of spiral worm round and through the machinery and cisterns, beginning at B C, and ending at the top of B¹ to I⁴, the number of revolutions being governed by the number of divisions in the racks D and D¹, so that if there were fifteen divisions in each rack there would be fifteen revolutions under C, round B, through G, under E, through D, and fifteen revolutions over C, round B¹, over I⁸, through D¹ and G¹, under E¹, over I², and again over C, passing from the top of B¹ to I⁴; and by this means, if one end of the goods marked K, and placed upon the series of rollers F, is fastened to the end of the guide cord, the goods will, when the calender is put in motion, be conducted and washed thirty times through the water in the cisterns, and squeezed thirty times through the calenders. As the operation proceeds and the guide-cord passes through the calender, it is wound by hand upon roller A to prevent it from becoming entangled, and to keep it in readiness for the next operation. As soon as the first end of the

FIG. 4.

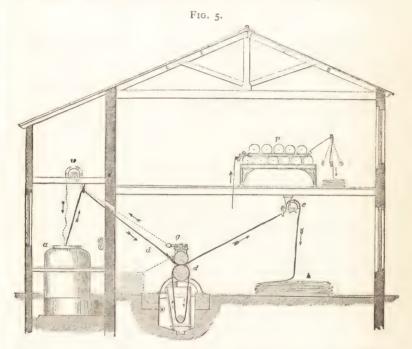


goods arrives at the guide-roller 1* it is detached from the end of the guide-cord and attached to the guide-cord at the other end, or with the opposite set of calenders. After this, by putting these in motion, the goods are washed and squeezed through its cisterns, supplied with hot and strong lime-lye, and the goods passing over guide-roller 1° are conveyed over other guide-rollers to be placed for the purpose, and taken down by some person or by proper machinery into one of the boiling vessels, where they are suffered to remain while the lime-boiling is effected.

The goods are saturated with the solutions by the aid of an apparatus shown in Fig. 4, being designed to supply continuous rapid motion and pressure to obviate the danger of rotting from still soaking. BBB are the washing rollers; CCC are the gear or speed rollers; EEE are rollers immersed in as many divisions of the cistern c, Fig. 3. The washing rollers, BBB (Fig. 4), are allowed to rise and fall upon the rollers CCC, according to the pressure exerted by the weights HHH. The goods having been steeped

are placed in batches at F, and passing under the immersing rollers, E, and the divisions of the cistern G, between the speed or gear rollers, C, and the washing rollers, B, are taken down straight and open into one of the vessels, and are then boiled by steam, which is succeeded by repeated washings alternately in water and bleaching liquors, until they are sufficiently bleached as before described.

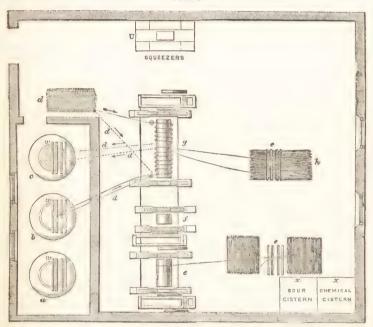
Figs. 5 and 6 show the elevation and ground plan of a bleach-house and machinery capable of working 800 pieces of 4 lbs. cloth per day, with the labour of one man and three boys, from four to six o'clock. d represents two lengths of cloth of 400 pieces each, passing through the washing machine, g, and from thence over the winch, w, into the kier, c, where they are boiled in



lime for twelve hours. They are then withdrawn by the same washing machine, g, washed, and passed into the second kier, b, where they are boiled for twelve hours in soda-ash and resin. They are again withdrawn by the same machine, g, washed, squeezed (see plan at u), and passed over winch, e, and piled at h. They are then withdrawn from the pile, h, and threaded the sour machine, e, soured, passed over winch e^a , and piled at k, where the cloth remains for three hours. It is then squeezed at u, and submitted to the washing machine, g, whence it is delivered into the third kier, a, boiled for six hours, again washed at g, and squeezed. It is then passed through the chemick, allowed to remain in pile for one hour; again soured, squeezed, and washed at g, again squeezed at f, and dried over the cylinders p.

The most important modifications of the continuous process of bleaching recently are those patented by Mr. Barlow in 1866. This inventor combines in one machine not only the various apparatus required for bleaching, but the operations successively of dyeing, printing, and sizing, subdividing the troughs or cisterns containing the mordants and the dyes by cross partitions, so that the





several threads passing through the machine at the same time may be dyed in different colours or partly left uncoloured.

These machines are, however, not adapted to the bleaching of linen. Linen does not possess the elasticity of cotton, and the strain would either pull the cloth narrow or tear it.

Bleaching with other Chemical Agents.

Several processes of bleaching with the aid of chlorochromic acid, chromates, chlorates, manganates, and sulphites have been from time to time introduced, but the operations have not been sufficiently successful or the use so extensive as to call for detailed description.

CHAPTER V.

LINEN FIBRE.

THIS fibre is obtained from the stem of an animal plant called Linum usitatissimum, belonging to the natural order of the Linnæ. Of what country it is a native is uncertain; but from its having been used by the Egyptians for mummy cloths, and that it is still found in those parts of Egypt which are inundated by the Nile, it is conjectured that it must originally have come to us from that country.

Three distinct varieties of flax are grown in Europe, viz., the cold or large flax, which has thin, tall stems, and yields a very fine long fibre, in great demand for the beautiful fabrics known as "Flemish Batist." This flax ripens earlier than the two other varieties.

The second variety is the hot or small flax, which yields a large quantity of seed (linseed), but its fibres are coarse and short.

The third variety, termed *middle-sized* flax, is the one most largely cultivated, and, as regards the fibre, most generally used.

Flax is grown in great abundance in Italy, Russia, Saxony, Holland, Belgium, and the northern parts of France. The fibre is separated from the plant in the following manner:—

The flax after being cut is allowed to remain in the field till it is dry. The seed is then beaten out, after which the flax undergoes a process termed retting, producing a peculiar fermentation, whereby the glutinous matters are destroyed, and the woody portions of the stem disintegrated; these portions being afterwards separated from the fibre by a mechanical process. Various propositions have been made at different times to substitute the use of chemicals for the retting process, which consists in steeping the plant in water; but it appears that the latter plan succeeds best. The water must be employed at a temperature of 96.8° F. (36° C.) The plants are placed vertically in tanks, so constructed as to admit of the water being renewed from time to time.

Viewed through the microscope, flax fibre exhibits hollow cylindrical tubes, open at both ends; the average diameter of these tubes is from 41 to 51 m.m.; their surface is smooth; septa or knots appear at intervals, but they are not furnished with hairy appendices, as is the case with hemp.

Bleaching Linen.

The flax fibre is surrounded by a somewhat thick incrustating matter of a yellowish grey colour, and consequently it is far more difficult to

bleach linen than cotton fabrics. Flax fibre being more susceptible of injury than cotton fibre, a more tedious bleaching process is necessary. It is conducted in the following manner:—The linen, instead of being steeped in hot or cold alkaline lyes, is first macerated in an infusion of malt at 149° F. (65° C.), after which mixtures of carbonated and caustic alkalies or resin-soap are employed at temperatures not exceeding 140° F. (60° C.); these are repeated after every washing and maceration. The linen is next exposed to the air on grass fields, and after the alkaline washings have been frequently repeated a weak solution of bleaching-powder is employed, followed by a sour-bath. It is impossible for linen to be thoroughly well bleached without frequent exposure to the air, and the expense attending these exposures partly accounts for the high price paid for linen as compared with cotton.

Such is the old method of bleaching linen, but later methods have been introduced in which the time of exposure on the grass, or "crofting," as it is termed, is much shortened. Dr. Ure very fully describes one of these processes as practised by an extensive bleacher in Scotland and Ireland, as follows:—

- r. Wash.
- 2. Boil in lime-water ten or twelve hours.
- 3. Sour in muriatic acid, of 2° Twaddle, for three, four, or five hours.
- 4. Wash well.
- 5. Boil with resin and soda-ash twelve hours.
- 6. Turn the goods, so that those at the top shall be at the bottom, and boil again as at No. 5.
 - 7. Wash well.
 - 8. Chemick at 1° Twaddle, or 1002'5 four hours.
 - o. Sour, at 2° Twaddle, 1010'o specific gravity.
 - 10. Wash.
 - rr. Boil in soda-ash ten hours.
 - 12. Chemick again.
 - 13. Wash and dry.

Other processes are adopted for sheetings, but, for printing, that quoted may be considered a fair example. By this process a fortnight is consumed in bleaching the goods. The continental processes are even still more tedious, occupying generally a period of six weeks.

White Bleaching Linen Yarn.

On the small scale the yarn may be boiled in a lye of soda-ash, or better, caustic soda, for about five or six hours; then taken out and rinsed; passed through a bath of chemick, when it will assume an egg-yellow shade. Then it must be rinsed, and crofted, or spread on the grass exposed to the sunlight; and if it is often wetted with water and turned it will become perfectly white in a few days.

Colouring Linen Yarn for Carpets on the Small Scale.

Coarse yarn is largely employed in the manufacture of special classes of carpets, and we append to the consideration of linen and its modes of bleaching some practical formulæ for the colouring of the yarn.

The yarn for blue, red, yellow, green, lilac, and aniline colours ought to

be bleached by taking it first through a warm bath containing a weak solution of chloride of lime, and then rinsing in fresh water. The yarn will still have a yellow appearance, but it will be bleached enough for the foregoing colours.

Yellow.

If there should be a variety of colours to prepare, it is better to commence with the yellow.

To 50 lbs. of yarn, bleached, boil for fifteen minutes-

1 lb. of flavine,

5 lbs. of alum,

4 lbs. of muriate of tin.*

2 ozs. of tin crystals.

Cool the dye to 170° F.; enter the yarn on poles, and turn it swiftly a few times; then slowly for twenty minutes. Take the yarn out, rinse in fresh water, and dry.

Green.

To 50 lbs. of linen yarn add to the above yellow dye-

5 lbs. of alum,

2 lbs. of muriate of tin,

2 ozs. of tin crystals,

4 ozs. of flavine.

The dye should be thoroughly mixed by boiling for ten minutes. When cool the bleached yarn is to be entered on poles, handled quickly at first, then slowly for twenty minutes, taken out and rinsed.

Now prepare a suitable tub with cold water, to which add a solution of 1 lb. of extract of indigo, and 6 lbs. of alum. The yellow rinsed yarn is now passed into this blue-bath, and turned quickly for a few minutes; then occasionally for a few hours, or until even, when it will be ready to be switched and dried, without rinsing.

Red.

To 50 lbs. of bleached yarn boil in the above yellow kettle for a few minutes—

5 lbs. of sumach,

I lb. of flavine.

5 lbs. of alum,

2 ozs. of tin crystals.

Then cool the kettle to 180° F.; enter the yarn, and handle it as usual for about fifteen minutes; then take it out. It is not necessary to rinse it; but

* Muriate of tin, otherwise scarlet spirit, as it is termed by dyers, is used as a mordant (spirit being a technical term for mordant), and the practical recipe for its preparation is as follows:—

16 lbs. of hydrochloric acid (22° B.),

I lb. of feathered tin,

2 lbs. of water.

The acid is poured into a stone pot, the tin at once added, and dissolved.

Tin Crystals are similarly prepared, only a larger quantity of feathered tin is added, the pot being placed on a sand-bath to facilitate solution, and the solution evaporated to crystallisation.

take now one pole after another through a small tub containing perhaps 6 pails of water and 3 lbs. of nitrate of tin.* Add a little nitrate of tin for every new pole taken through, and handle each pole in the mordant for one and a half minutes. It is cheaper to have a small tub for this bath, as the yarn can be then strongly mordanted, which is necessary to obtain a good red. Place a board on the top of the side of the tub, so that the liquid will run back from the yarn laid upon the board to drain. Next prepare a kettle with warm water at 125° F., and add the infusion of 15 lbs. of common peachwood.† While stirring, enter the prepared yellow yarn, turning it quickly two or three times, and then slower for twenty minutes, when it will be of a fine red. The red can still be improved by adding 2 lbs. of wbiting to neutralise the acid. The acid must be rinsed from the yarn before the latter is dried.

Orange, with Madder.

To 50 lbs. of yarn, bleached, add to the yellow kettle above-

I lb. of flavine,

5 lbs. of alum,

2 lbs. of muriate of tin,

2 ozs. of tin crystals,

5 lbs. of madder.

This kettle must be boiled for ten minutes, and then cooled to 170° F. The yarn is now to be entered, turning it quickly a few times to obtain evenness, then slowly for about fifteen minutes. It can be then removed, rinsed, and dried.

Orange, with Annatto.

This orange is brighter on linen than the one just described with madder, but the colour is not so fast.

For 50 lbs. of bleached yarn. Boil r lb. of annatto with 4 lbs. of soda-ash, pouring the whole into a kettle of hot water of 160° F. Enter the yarn and handle for fifteen minutes, rinse, and dry.

Brown and Maroon.

Pass 50 lbs. of dry yarn, unbleached, through the yellow kettle, handling for fifteen minutes. After removal mordant the yarn with nitrate of tin as for red; next enter it into a kettle containing the liquor of 10 lbs. of peachwood with 10 lbs. of logwood, handling for twenty minutes; rinse and dry. For maroon more peachwood and less logwood will be required.

Crimson.

For 50 lbs. of bleached yarn. Take the yarn through the liquor of 10 lbs. of boiled sumach; next through the cold nitrate of tin mordant, thoroughly

- * Nitrate of tin may be prepared thus:—To 5 lbs. of hydrochloric acid (22° B.), 10 lbs. of nitric acid (36° B.), 5 lbs. of water; add 1 lb. of feathered tin in very small quantities at a time to the acid so as not to overheat it.
- + Peachwood liquor is sometimes termed, chiefly in America, hypernic. This term is derived from Nicaragua (Nicaragua wood), whence "Nicric," a superior quality of liquor from the same wood being termed "hyper-nic.'

impregnating the yarn. Then pass it into a warm beck (140° F.) containing the boiled liquor of 15 lbs. of peachwood. After twenty minutes rinse and dry.

Pensée Brown.

For 50 lbs. of dried yarn. To a kettle of water at 140° F. add-

5 lbs. of alum,

10 pails of logwood liquor (2 lbs. to the pail),

5 lbs. of nitrate of tin.

The yarn must be handled for twenty minutes, rinsed, and dried. To render the colour more even the yarn may be taken through the alum and logwood liquor first, then removed, the nitrate of tin added, and the yarn re-entered and finished.

Magenta.

For 50 lbs. of well-rinsed yarn. Dissolve 1½ ozs. of magenta crystals in hot water, and add the solution to a warm beck at about 150° F. The yarn should be entered and handled thoroughly for twenty minutes, the beck being well stirred. Switch and dry without rinsing.

Aniline Purple.

For 50 lbs. of well-rinsed bleached yarn. Dissolve 2 ozs. of aniline purple in 1 pint of hot alcohol, and add the alcoholic solution to a bath of warm water at 140° F., next adding 4 lbs. of acetic acid. Handle the yarn in this beck until the colour has become even; rinse and dry.

Aniline Blue.

For 50 lbs. of bleached yarn. Dissolve 4 ozs. of aniline blue powder in 1 pint of hot alcohol, adding the solution to a kettle of warm water at 140° F., together with the solution of 3 lbs. of Glauber salts, and 2 lbs. of acetic acid. The kettle must be heated to nearly the boiling-point while handling the yarn. After twenty minutes remove, rinse, and dry.

Prussian Blue.

For 50 lbs. of bleached yarn. A beck, slightly warm, must be prepared with 3 lbs. of nitrate of iron,* to which should be added 2 lbs. of muriate of tin. The yarn having been turned five times in this iron bath, should be removed and passed through a second bath, consisting of the solution of 2 lbs. of yellow prussiate of potash with 1 lb. of sulphuric acid. After draining for a few minutes, pass the yarn again through the iron bath. If the colour be desired darker, handle once more through the prussiate bath. Then rinse well, and dry.

Lilac.

For 50 lbs. of bleached yarn. Have in readiness 2 pails of a warm infusion of logwood, to which add 4 lbs. of alum and 2 lbs. of muriate of tin. Handle the yarn for twenty minutes, remove, and rinse.

* Nitrate of iron may be prepared as follows:—To 5 lbs. of water in a stone vessel add 2 lbs. of hydrochloric acid (22° B.), and 10 lbs. of nitric acid (36° B.) In this acid solution wrought-iron chips are dissolved, care being taken not to add iron in excess. When sufficient iron has been dissolved, or the acid is nearly saturated, 5 lbs. of copperas are to be added. When the copperas is dissolved the mordant is ready for use.

Bismarck.

For 50 lbs. of bleached yarn. Form a beck with 5 lbs. of boiled madder, to which add a solution of 5 lbs. of alum, heating the beck to 150° F. Handle the yarn for five turns; then add to the beck 2 lbs. of muriate of tin; handle for fifteen minutes, rinse, and dry.

Slate.

For 50 lbs. of bleached yarn. Pass the yarn through a warm bath, containing 5 lbs. of boiled sumach and 1 pail of logwood liquor, giving the yarn six turns. Then remove the yarn, and pass it through a cold solution of 2 lbs. of copperas and ½ lb. of blue vitriol. After twenty minutes rinse and dry.

Cutch Brown (fast).

Take 50 lbs. of dry yarn through a hot beck containing the solution of 10 lbs of cutch; or the yarn may lie in the beck over night. Then remove the yarn and handle it through a hot solution of bichromate of potash. Rinse and dry.

Black.

For 50 lbs. of yarn. Have in readiness a kettle containing 10 pails of logwood liquor, to which add 2 lbs. of blue vitriol and 2 lbs. of soda-ash. When these are dissolved, cool the kettle to 180° F., enter the dry yarn, and handle it for twenty minutes. Then remove, rinse, and dry.

Another Black, a Fast Colour.

For 50 lbs. of dry yarn. Soak the yarn overnight in a warm solution of 15 lbs. of sumach. The next morning remove the yarn, and pass it through a warm solution of 5 lbs. of copperas, 1 lb. of blue vitriol, and 2 lbs. of whiting. Then handle it through a cold weak lye of lime-water; rinse the yarn, and again pass it through the sumach bath, to which has been added 6 pails of logwood liquor and 1 lb. of boiled starch. The latter will precipitate all the dye-stuff upon the yarn, and a good black, perfectly fast, will be obtained.

CHAPTER VI.

HEMP, CHINESE GRASS, JUTE, AND OTHER FIBRES.

HEMP is the fibre of an annual plant known as Cannabis sativa, originally found in Asia. It has, however, been cultivated in Europe for many centuries. This plant attains a height of from 1'3 to 2'6 metres, and, as in flax, the fibre runs through the entire length of the stem. It is both separated from the plant and bleached in a similar manner to flax, but the bleaching is more difficult on account of the greater quantity of incrustating matter that surrounds the fibre. Seen through the microscope, the hempen fibres exhibit hollow cylindrical tubes, quite smooth externally, and provided at regular intervals with septa or knots, surrounded by small hairy appendices. Hemp fibre averages 210 to 310 of a millimetre in diameter. It is chiefly employed in making rope, twine, and sail-cloth, and consequently is rarely dyed or bleached.

The other fibrous materials known to us may be divided into three kinds, viz., those obtained from the stems of plants, those from the leaves, and those from the nutshell.

To the first division belongs the so-called Chinese grass, the fibre of a plant included in the natural order of the *Urticacea*, more particularly the *Boehmeria nivea*, cultivated to some extent in China. The fibre when woven to tissue constitutes the China grass cloth, but it is not used to any great extent either in Europe or Asia.

Ramee hemp is made from the fibres of the *Urtica utilis*, a native of Borneo, Sumatra, Java, and some of the smaller Sunda Islands. These fibres average about 1.5 to 2.2 metres in length. They are naturally of a bright yellow-white colour, readily bleached to a very perfect white, but are not much used on account of an inherent stiffness, which, as far as present experience goes, cannot be removed. The natives make cordage of the fibre, but it is of inferior strength, and does not well resist the action of sea-water.

Rhea hemp from the Rhea tenacissima, East Indies, is used very little even by the natives.

Jute, the fibre of the Corchorus olitorius, together with the other species of the same family, is, with the exception of hemp, used more largely than any of the fibres referred to; it is not, however, suitable for making cordage, as it breaks too readily, and rots under water, but it is extensively used for sail and other coarse cloth. Its finer fibres are, it is stated, woven into such fabrics as poplins and mixed reps. Jute is also used by hatters, as it will take a good black dye.

Bombay hemp is the fibre derived from the Hibiscus cannabinus; its use is, however, very limited.

Amongst the fibres obtained from leaves those chiefly in use are:—New Zealand flax, the fibre from the *Phormium tenax*. This fibre is very strong, especially in its crude state, but it is very difficult to bleach. The plant could very well be cultivated in Europe, but as the process by which the fibre is obtained is a tedious one, and its natural colour a light cinnamonbrown, it is not favourably received. A gummy juice is obtained from this plant, which is beginning to be used for rendering envelopes adhesive, as paper fastened by it cannot be opened either by damping or steaming.

Several species of the Agave tribe yield fibres which are sometimes used, but they are not well known in Europe.

Manilla hemp is the fibre derived from the Musa textilis, and other species of the same family. This fibre is brought to Europe, and, mixed with hemp, is made into rope, twine, sacking, &c. The leaves of the Bromelia ananas (the pine-apple plant) contain fibres of great comparative whiteness, but even in such countries as Mexico, where the pine-apple is so plentiful as occasionally to be used as fuel, the extraction of the fibre from the leaves is not attempted to any great extent, the difficulty of getting rid of the concomitant vegetable matter being too great, especially as cotton can be grown there, and in most of the countries where the various fibres alluded to are produced.

Coir, or cocoa-nut fibre, is obtained from the exterior shell (pericarpium) of the fruit of the cocoa-nut palm. It is used in its unbleached natural state for making matting, &c.

Very little is known about the action of dyes on these fibres; some of them are never dyed; even linen (flax fibre), which after bleaching is pure cellulose, does not take some colours so well as cotton.

CHAPTER VII.

THE MEANS OF DISTINGUISHING VEGETABLE FIBRES FROM EACH OTHER.

As the fibres when thoroughly bleached are almost pure cellulose, it is evident that chemical tests cannot be applied for the purpose of distinguishing one kind from another; but as the incrustating matter can never, on a large scale, be entirely removed, it is possible by chemical tests to distinguish between flax and cotton, the two principal vegetable fibres.

Messrs. Bættger and Kuhlmann employ for this purpose the yellow-orange colour caused by the action of caustic alkalies on these fibres. M. Bættger immerses the materials to be tested in a boiling solution of equal parts by weight of water and caustic potassa; they are allowed to remain in this solution for about a minute, when they are removed and placed between sheets of blotting or filtering paper, and the excess of liquid expressed. Flax fibre or linen assumes a dark yellow colour, while cotton either remains white or becomes a very bright yellow. According to M. Kuhlmann, raw cotton, when placed in a very concentrated but cold solution of caustic potassa, becomes bright grey, while flax under the same conditions assumes an orange-yellow colour, which is probably due to the presence of pectic substances, pectine or pectic acid.

M. Kindt states that strong sulphuric acid at the ordinary temperature destroys cotton far more rapidly than it does hemp or flax.

When cotton and flax or their tissues are immersed in oil and strongly pressed in order to remove the excess of the liquid, the cotton remains opaque, while the flax becomes transparent.

New Zealand flax may be distinguished from ordinary flax or hemp by the fact that on being immersed in nitric acid of 36° Baumé containing nitrous acid in solution, it assumes a red colour, or, if it is first immersed in strong chlorine water and then in ammonia, a reddish tint is imparted, which is not the case with hemp or flax grown in this country. The best means, however, of distinguishing the different fibres is to examine their minute structure by the aid of the microscope; in this way reliable results are obtained.

CHAPTER VIII.

VEGETABLE THICKENINGS.

THE principal substances used as thickeners are starch, fecula, flour, various kinds of disintegrated starch, such as roasted starch, leïocome, dextrine, gommeline, gomma, the gum produced by cherry and plum trees, the genuine gums, such as arabic, senegal, tragacanth, Bassora gum, salep, sago, linseed, and carragheea. All these substances are, in chemical parlance, carbo-hydrates; their formula is typified by that of cellulose, with which they have many properties in common.

Amylaceous Matters-Starch, Fecula, C6H10O5, or C12H20O10.

Amylum, that is, grain which needs no grinding, is a very common constituent of the entire vegetable kingdom. It exhibits an organised substance of globular shape, the size of the globules varying with the species of the plant from which it is produced. Every grain is composed of concentric layers of different densities, superimposed one upon another. In the centre a small nucleus may be seen by the aid of a microscope, which serves as a common centre for the different layers. The peculiar construction of the starch globules is seen to greater advantage after the substance has been heated to 392° F. (200° C.) and then swollen by immersion in water. The shape of these globules is polyangular. Their size varies considerably; expressed in thousandths of a millimetre it is as follows:—Canna gigantea, ovoid shaped, 175 diameter; Solanum tuberosum (potato), ovoid, 183 diameter; beans (cotyledons), oblong, 75 diameter; wheat, and similar kinds of grain, spherical, 45 to 50 diameter; sago, a flattened ovoid, 35 diameter; for Zea Mais (Indian corn) a rounded polyhedron, 24 diameter; the seed of Chenopodium quinoa, globular, 2 diameter.

The amylaceous matter is enclosed in cells while in the living plant, and is found in abundance, together with more or less nitrogenous matter, in the trunks of many kinds of palm trees, in the perispermium and cotyledons of seeds, more especially beans, peas, and the various kinds of grain; in the roots, tubers, and bulbs of plants, as, for instance, in carrots, rhubarb, liquorice, manioc, potatoes, florentine iris, bryonia, tulips, &c.; in some fruits, as acorns, chestnuts, buckwheat, &c.; it is also found in many kinds of lichens.

Starch is used only in the pure state, as obtained from wheat, rice, potatoes, chestnuts, Indian corn, and the various kinds of arrow-root, with all which vegetable substances it is intimately associated. The methods by which starch is prepared are based upon its insolubility in cold water, together with its comparatively high specific gravity, and its resistance to the action both of weak acids and alkalies, and also to putrefactive fermentation at the

ordinary temperature of the air. The manufacture of starch may therefore be considered as a process of mechanical separation, aided by weak solvents of an acid or alkaline nature. It is very hygroscopic, and may retain even as much as 45 per cent of water (the so-called green starch); but in dry starch the quantity of hygroscopic water generally varies from 3 to 16 per cent. In a perfectly dry and pulverulent state starch exhibits a very mobile powder, devoid of smell, taste, and colour. It is, as far as any practical purposes are concerned, insoluble in cold water; but some chemists and botanists aver that when starch is rubbed for some time in a mortar with very sharp sand and cold water, and then filtered, a clear solution is obtained, which is coloured blue on the addition of tincture of iodine, and is precipitated by alcohol and subacetate of lead. In this case every granule of starch should consist of an insoluble and a soluble portion, both isomeric as regards their chemical constitution. This view is strongly supported by the experiments of M. Béchamp, who has succeeded in effecting a molecular transformation of starch, whereby it is made completely soluble, while it retains the property of becoming blue on the addition of iodine. This transformation is effected-(1) By heating starch and monohydrated acetic acid to 212° F. (100° C.); (2) By acting upon starch with ordinary acetic acid, and with concentrated sulphuric and nitric acids; this operation requires great care; (3) By reducing xyloïdine or nitramadine by means of chloride of iron. This intermediate state being the first stage in the conversion of starch into dextrine, by careful management this so-called soluble modification of starch may be obtained in all cases where its conversion into dextrine takes place. By polarised light soluble starch exhibits a very marked right-handed rotation of the ray. When starch is made into gum (dextrine) by roasting, and this gum viewed under the microscope with a power of about 300 diameters, after having been moistened with alcohol, the granules remain perfect, the hilum only appearing a little more marked; but when to the dry gum water is added the granule cracks at the hilum, and the dextrine may be seen oozing out rapidly into the water. The empty starch envelopes may then be seen floating about, very light, retaining the general appearance of the original granule, but with a large aperture with ragged edges where the dextrine has escaped. These envelopes give no colours when viewed with polarised light. The action of boiling water upon starch is simply a disintegration, not a solution, as is proved by the opalescence of the liquid after the addition of a quantity of boiling water, and also by the fact that, on being frozen and again becoming fluid, the whole of the starch is precipitated, and the supernatant liquor on being carefully decanted does not become blue when a solution of iodine is added. A most interesting phenomenon is the conversion of starch into dextrine and sugar under the agency of certain bodies, which, according to Berzelius, appear to act catalytically; that is to say, they induce a molecular conversion, and also, as regards the sugar, the taking up of a molecule of water or hydratation at the same time. Dextrine has exactly the same composition as starch, while glucose differs from it by containing another atom of water. Starch is converted into either dextrine or glucose by the following reactions:-(1) By the action of pure water at a temperature of 302° F. (150° C.), which if sufficiently prolonged produces glucose; (2) A dry heat of 392° F. (200° C.) converts starch into dextrine only; (3) When to boiling water two or three hundred parts of its weight of sulphuric, hydrochloric, or any other strong mineral

acid is added, and starch (not green starch) previously made into a paste with water is poured into this liquid, which must be kept boiling, the starch is first converted into dextrine, and afterwards into glucose; (4) The peculiarlymodified nitrogenous principle met with in malted barley, generally called diastase (though Professor Mulder proved some years ago in his excellent work on Beer that diastase individually does not exist at all, and that the incipient germination of barley or any other grain has the effect of greatly modifying the composition and action of the protein compounds met with in grain) has the power of converting starch into dextrine and glucose at a temperature not exceeding 167° F. (75° C.), and to act thus even in relatively small quantity, since one part of the nitrogenous principle readily converts a thousand parts of dry starch into dextrine, provided sufficient water be present; saliva, pancreatic juice, bile, and intestinal mucus of men and animals act in a similar manner, and are very rapid in their action. Iodine in free state gives to starch paste a beautiful deep blue colour, which disappears on the application of heat, but the action of this well-known reagent is either entirely or in part prevented by the presence of some substances, among which, according to Goppelsroeder, are many soluble sulphates. If, when dry starch and strong sulphuric acid are mixed at the ordinary temperature of the air, an amylosulpho-acid is formed, at a higher temperature the starch is decomposed and becomes black; it is converted into xyloïdine at the ordinary temperature by the action of very strong nitric acid, and, at a higher temperature, into oxalic acid. Starch-paste, when exposed to the action of air, is gradually converted into lactic acid. Schweitzer's reagent does not affect starch. When of good quality starch contains but little ash, for the incombustible matter that may be present being only that which was found as solid residue after the evaporation of water, is, therefore, attributable to the water employed in the manufacture of starch. It sometimes happens that starch is purposely adulterated with gypsum, sulphate of baryta, or prepared chalk, but such frauds are readily detected by incineration. Starch (fecula) is very largely used, especially in the dressing of goods; it is applied either with or without dextrine to thicken colours for printing; sago, wheaten flour, wheaten starch, farina, and salep are all thickeners of the same class.

Dextrine.

We have already alluded to the method by which dextrine is manufactured, but it is necessary to mention here that since the colour of what is now called calcined farina was, in many instances, an objection to its being used in calico printing, it was very desirable to find a process for its conversion at so low a temperature as to leave the converted farina nearly colourless. This was first effected in 1838 by M. Payen, who found that by adding 400 parts of dry farina to I part of nitric acid at a specific gravity of 1.4, diluted with sufficient water to form with the farina a hard paste, this being dried slowly and heated in a close chamber for twenty hours at a temperature of 392° F. (200° C.), a nearly white farina was obtained. It is interesting to observe how so small a quantity as a few thousandths of acid can effect this great molecular change. Since that time many processes have been devised to attain the same end; such, for instance, as the employment of lactic acid by Mr. E. Hunt, of oxalic and tartaric acids by others, and a process by Mr. Charles O'Neill, which

GUMS. 69

is valuable, as it enables him to convert insoluble into soluble farina or dextrine without any change of colour. This he effects by subjecting starch, farina, and other amylaceous substances to the chemical action of hydrochloric or some other acid gas or vapour in a cylinder, the exterior of which is surrounded by an atmosphere of steam. This process cannot be said to have materially extended the employment of soluble farina as a substitute for gumarabic, as perfectly soluble white dextrine is easily made on the large scale by Payen's process without needing the expensive apparatus used by O'Neill.

Calico printing, as at present developed, having assumed such extraordinary proportions, thousands of tons of soluble materials for thickening the various mordants and colours are required, and a great variety of this class of artificial gums are prepared to meet the requirements. Thus, in addition to farina, sago, rice, slimes, and wheaten starch are used. The latter substance when heated generally bears the name of British gum, which differs from calcined farina in being soluble in boiling water only. Pure dextrine exhibits the following properties: - In the dry state it is as white as powdered gum arabic; it has a slightly sweet taste; it is soluble in water in all proportions, yielding, according to the proportion of water present, a more or less viscous solution; insoluble in alcohol, by which it is precipitated from its aqueous solution as a flocculent mass; it gives a strong right-handed rotation to polarised light, hence its name. Nitric acid and heat convert it into oxalic acid, while the native gums are chiefly converted thereby into mucic acid. Solution of neutral acetate of lead does not precipitate a solution of dextrine unless ammonia be added, but it is precipitated by subacetate of lead; it is also precipitated by chloride of tin, but not by solutions of salts of peroxide of iron. Solutions of iodine impart no colour to dextrine. A hot alkaline solution of oxide of copper is reduced by dextrine, but not by native gums. Commercially, it is distinguished as calcined farina, starch heated to 392° F. (200° C.), leïocome, roasted wheaten starch, gomma, gommine, and gommeline, all of which are dextrine, more or less pure, and varying in colour, and are prepared by the action of acids and heat upon starch, as already described.

It should be borne in mind that starch and wheaten flour, with all the substances derived from them or manufactured with them, exert a reducing action, preventing oxidation of the colours. Colours mixed with dextrine do not keep so well as those mixed with gum.

Gums.

Four kinds are chiefly used—(1) Soluble gums (arabic, senegal, and salabreda); (2) Gum tragacanth; (3) Bassora gum; (4) Inland gum (the gum from cherry, plum, and other stone fruits). Only the first two of these kinds are used as thickeners.

Gums Soluble in Water belonging to the species of Arabic Gums.

—There are three varieties in the market—Arabic, senegal, and salabreda; these all exude from trees belonging to the Acacia tribe.

Without practical experience it is very difficult to distinguish between the three above-mentioned varieties: gum arabic dissolves more readily in water, and, as its solution has less tendency to become acid, it is better suited as a thickener for bright and clear mordants; but, on the other hand, its solutions are more readily coagulated by basic metallic salts than those of

senegal gum. The solution of the latter gum in water is at first quite colourless, but in a few hours it becomes very dark, sometimes as dark even as an aqueous solution of Spanish juice. These gums contain a peculiar principle, which is known as arabine, and also a very small quantity of an organic lime salt, and variable quantities of chlorides of calcium and potassium and acetate of lime. Arabine is insoluble in alcohol, and even in weak spirits. Aqueous solutions of gum are therefore precipitated by these fluids, and also by solutions of persalts of iron, nitrate of mercury, subnitrate and subacetate of lead. The precipitate contains gummic acid combined with metallic oxides. Boiling nitric acid converts gum into oxalic, tartaric, and mucic acids. Solutions of gum turn the plane of polarisation to the left. Allowed to remain, they are gradually converted into glucose. The solutions of all varieties of gum very soon become acid, a fact of some importance in reference to the use of gums as thickeners. When gums are boiled for some length of time with dilute acids, glucosic acid is formed. The soluble gums do not reduce the potassio-tartrate solution of copper unless they are heated for some time with water either in sealed tubes or in a Papin digester at a temperature of 302° to 320° F. (150° to 160° C.)

Gum Arabic.—East Indian gums and an Australian article are largely used for manufacturing purposes, and these, together with samples of picked gum senegal, are substituted for the genuine gum arabic, which has become too

scarce to be used as a thickener.

Gum Senegal is chiefly used as a thickener; it is dissolved in water at 140° or even at 212° F. (60° or 100° C.), and allowed to stand till the impurities have settled, when it is passed through a fine hair sieve. It is employed especially in printing with rollers. Gum solutions do not mix readily with other thickeners; with pipe-clay there is, however, an exception. It happens occasionally that larger or smaller quantities of gum, insoluble in water, are found among the soluble gums; when this is the case the material swells in water, but does not yield a clear liquid.

It is worthy of observation that gum neither tarnishes nor alters delicate colours, nor weakens the mordants; that it does not coagulate colours, and that on being dissolved in water it thickens rapidly. The action of gums upon delicate colours is best tested with cochineal pink or fuchsine upon pure wool; after impression, the colour is steamed, and then washed, and if the

gum is pure there will be no trace of any yellow tinge or hue.

The action of gum upon mordants varies greatly, and depends very much upon the degree of acidity of the aqueous solution. For certain colours it is therefore absolutely necessary to use a very superior kind of gum; this applies especially to bright pink and rose-red. In order to estimate the dissolving action exerted by gum upon mordants, an impression is made with a mordant for bright rose-red, thickened with the gum to be tested. A fabric mordanted with this mixture after having been treated in the usual way, which is hereafter described, is placed in a madder-bath and cleansed with soap, when it should produce a bright rose-red; if the gum be acid there is hardly any mordant left, and consequently no effect of dye is afterwards to be seen.

Gums should possess the property of giving to water a certain degree of viscosity without requiring an excess of material: this point is of far greater

GUMS. 71

importance than is often imagined; for, supposing a manufacturer to require annually a given quantity of gum of first rate quality, and to pay for that quantity, say £3520, if the viscosity of the gum were reduced by one-tenth, it is clear that this would necessitate an outlay of £352 more. Several instruments have been devised for measuring the viscosity of solutions of gum and other viscous materials, and of these the least expensive and most simple appears to be a glass funnel, the tube of which is drawn out to a fine point. Solutions of gum are made in definite proportions, and the funnel having been filled, the time that the several solutions take to run through is accurately noted, this operation being shorter or longer according to the degree of viscosity of the solution under treatment. M. Steilmann's viscosimeter consists of two hollow glass cylinders, placed side by side, one of which is filled with pure water, and the other with the solutions to be tested. Into each of these cylindrical glasses (which are precisely similar) metallic balls can be let down. These balls are suspended by silk threads, and move freely over pulleys; they are, however, partly counterpoised by means of weights. If the viscosity of the liquids placed in the glass cylinders be equal, the metal balls will descend with the same speed, provided, of course, that they are of the same size and weight; but if one of the cylinders contain water, and the other a solution of gum, the ball will sink into the latter more slowly than into the former. The descent of the balls, when nearly at the bottom of the cylinder. is stopped by a peculiar mechanical arrangement. M. Steilmann's apparatus is in many respects an excellent one, but it is too complicated to be of great practical use to those who require to test several samples of gum in a short space of time. It should be borne in mind that although a solution may be made of accurately weighed quantities of gum and water, the degree of viscosity of such a solution is affected by the temperature of the water and of the room in which the experiment is made. It is therefore necessary that these experiments should always be made at the same temperature, 59° F. (15° C.), and it is also advisable to be provided with a freshly-made solution of best quality gum that may be used as a standard of comparison.

Gum Tragacanth is the produce of the Astragalus verus, a tree growing in Persia, Armenia, and Asia Minor. It is a white or yellow looking substance, and is not really soluble in water, as it only swells in it, yielding a thick mucilage. It contains on an average about half its weight of soluble arabine, but consists principally of what is often called bassorine. Gum tragacanth always contains some starch. Before being used it is soaked in cold water for twenty-four hours, and afterwards boiled from four to six hours until a thick homogeneous solution is obtained. The quantity of gum to 35 ozs. of water varies from about 930 to 1530 grs. Though the solution made as described is very thick and nearly colourless, it is less cohesive than gum solution, and cannot therefore replace it. When gum tragacanth is boiled with water, under a pressure of from four to five atmospheres, it yields in about twenty minutes a thick solution. To test the viscosity of this gum 279 grs. are taken upon 17½ ozs. of water; the fluid is boiled, and when it has cooled down to 59° F. (15° C.) its viscosity is compared with that of a solution of the same strength made from a good sample of the gum.

The mucilage produced by steeping linseed, the seeds of quinces, and carragheen moss for some time in warm water, also affords a thickening

material, but it cannot correctly be called a solution, and the mucilage is rather pectine than true gum.

It is very difficult to give precise directions as to the quantity of thickening required for the preparation of the colours, as this depends partly on the viscosity of the thickeners themselves, and still more on the chemical action exerted upon them by the colouring matters. For instance, where a certain quantity of starch is sufficient for indifferent (neutral) solutions, or such as become only slightly acid after boiling, half that quantity will suffice when those salts are employed which exert a coagulative action, such as concentrated solutions of sesquioxides, or caustic substances like soda. With sulphates the result is different.

When gum is used a small quantity is generally sufficient with the larger class of mordants (the solutions of sesquioxides), but double the quantity will be found necessary for indifferent solutions, proto-salts, &c. The more basic any salt is, the greater is its tendency to coagulate; the sesquioxides have this tendency, but the proto-salts have not. Those substances which possess the greatest thickening power, such as gum tragacanth and starch, are not so suitable for printing purposes as the natural and artificial gums, which are viscous and fluid at the same time.

We may here observe that gum acts in a peculiar manner with the acetate mordants; for instance, with proto-acetate of iron it has the effect of producing paler tints than roasted starch. This peculiarity, which is generally believed to be due to the acidity of gum solutions, appears, according to M. C. Kœchlin, to be simply a hygrometrical effect, as when glycerine or sal-ammoniac is added to the pigment mixed with gum solution, the latter is restored to all its superiority of action.

CHAPTER IX.

ANIMAL FIBRES. THICKENINGS OF ANIMAL ORIGIN.

THE classification of fibres according to their origin is important in a scientific point of view, as it is based upon a difference of chemical composition. A similar link of connection exists between wool and silk as there does between hemp, flax, and cotton, the latter being intimately allied to the neutral carbo-hydrates, while silk and wool belong to the nitrogenous albumenoid substances, which sometimes contain sulphur as well as nitrogen.

We are here led by analogy to the consideration of albumen, caseine, gluten, fibrine, and gelatine, all of which now play an important part in the fixing of colouring matter and pigments to woven tissues.

Albumenoid Substances.

These are very widely dispersed both in the vegetable and animal kingdoms, though they are often considered to belong chiefly to the latter. The number of these bodies is very large, but their characteristic differences are not great. The chief substances of this kind which demand attention in this work are albumen, fibrine, gluten, and caseine, to which is often added the diastase of malt, diastase being the name given to albumen in that state in which it effects the conversion of starch into dextrine and cellulose. The plastic substances of the animal organism, as, for instance, that membranous secretion called wool, the fibroine of silk, gelatine, and the tissues which yield gelatine, on being boiled in water, are in some respects similar to the albumenoid substances; they differ from them, however, sufficiently to admit of a separate classification.

The following table exhibits the composition of the most prominent of these substances, many of which are only molecular modifications of each other:—

	Albi	men, Fibrine, Caseine.	Epidermic Productions.	Gelatine yielding Tissues.	Fibroine.
Carbon		53.2	50.6	49*38	50.2
Hydrogen		7.1	7.0	6.21	7.0
Nitrogen		15.8	17.5	17.60	18.0
Oxygen		10.8	22.6	26.20	24.5
Sulphur		1.8	2'3	0.00	0.0

The albumenoid substances are generally solid, and not capable of assuming a crystalline shape: the protein substance of the blood globules has occasionally been seen in a crystalline state. As to their solubility in water, this seems to depend entirely upon certain salts or acids with which they are combined;

in a pure state they do not appear to be at all soluble in pure water. Under the combined influence of heat and moisture, or of mineral acids and some metallic salts and organic compounds, these substances are converted into allotropic modifications, whereby they become insoluble. Albumenoid substances, as a rule, are not soluble in alcohol, ether, or neutral organic liquids. Exposed to a high temperature (that is to say, below red heat), these compounds become decomposed, swell up, and fuse, yielding on dry or destructive distillation a very large number of rather complex compounds according to the degree of heat applied. Among these products we find sulphuretted hydrogen gas and hydrosulphide of ammonium, ammonia, carbonate of ammonia, aniline, picoline, pyridine, toluidine, pyrrol, methylamine, propylamine, and tetrylamine. A portion of the nitrogen combines intimately with the carbon, yielding a nitride of carbon formerly employed in the manufacture of cyanides. Water, carbonic acid, neutral oxygenated principles, and hydrocarbons are simultaneously formed.

Albumenoid substances are more or less readily soluble in weak aqueous solutions of caustic alkalies. The quantity of caustic alkali should be very small, for if the solution be even as weak as 2 per cent of solid hydrate, a decomposition of the albumenoid matter ensues in most cases, and minute quantities of sulphuretted hydrogen are given off. These solutions are precipitated by acids, but the precipitate does not necessarily re-constitute the identical substance. When heat and stronger alkaline solutions are simultaneously applied, ammonia, organic alkalies, carbonic and formic acids, leucine, tyrosine, gelatine, and sugar are generated. When these substances are fused with alkalies, an alkaline cyanide is obtained. The albumenoid, called also protein, substances combine with both acids and alkalies, yielding, with the former, compounds which are insoluble in acidulated water, but soluble in pure water.

Concentrated acetic and other organic acids, and the hydrate of the tribasic phosphoric acid dissolve albuminous substances; these solutions are precipitated by an aqueous solution of ferrocyanide of potassium, which does not precipitate the solutions in these same acids of gelatine and gelatineyielding tissues. Concentrated hydrochloric acid aided by heat yields with the albumenoid substances, provided air be admitted, a solution which assumes a rich blue-purple colour. Nitric acid has the effect of colouring these substances deep yellow, owing to the formation of xanthoproteic acid, which, on the addition of ammonia, assumes an intense orange colour. This property of nitric acid is turned to account in the production of beautiful and fast yellow and orange colours in woollen and silken fabrics and in feathers. A solution of mercury in nitric acid (1 part of metal and 2 of nitric acid at 36° B.) yields, when heat is applied, an intensely red colour with all albumenoid substances. These bodies are coloured deep brown with iodine. oxidising agents, such as chromic and permanganic acids, and a mixture of sulphuric acid and peroxide of manganese, act very energetically upon the albumenoid substances, producing a great many homologues of the fatty acid series (C_nH_{2n}O₂) and the corresponding aldehydes; also benzoic acid, hydruret of benzoyl, hydrocyanic acid, and the cyanides of methyl, ethyl, &c.

Ozone also acts upon some of these substances in a peculiar manner. When albumenoid substances come into contact with air and moisture at a sufficiently

elevated temperature they undergo decomposition, which is accompanied by the emission of fœtid gaseous products. That absolute absence of moisture prevents, to a great measure, that decay which is termed slow decomposition is instanced in the preservation of the bodies of the dead monks in the vault of the church at the Kreuzberg, near Bonn; also of some bodies found in a vault of the ancient church of St. Michel, at Bordeaux; as well as by similar effects in the leaden vault of the principal church at Bremen, and in the vault under the choir of the church at Wienwert, a small village near Bolsward, in Friesland. While in proof that there is no decay at lower temperatures than o° C., may be cited the occurrence of the mammoths found in ice in Siberia in a state of perfect preservation. The hair, nails, hoofs, horn, and wool and silk, resist; decomposition for a long period, the resistance being due partly to the small quantity of water which they contain, and which can be expelled at 100° C. (212° F.) According to M. Pasteur, this putrefaction, as it is genetically termed, is due to the development of infusoria and vibrios, the germs of which are conveyed by the air. Putrefaction may be entirely prevented, besides, by the actions already mentioned, by the exclusion of air, and by the destruction by means of heat of the pre-existent germs. Some substances known as antiseptic possess the property of arresting and preventing decay, and consequently putrefaction. Among such substances are the metallic compounds of copper, mercury, and arsenic; the sulphites and chlorides of sodium and potassium; and among organic substances tannin, carbolic acid, alcohol, &c. Gelatine, for instance glue, unless it is dry and is maintained in a dry state, putrefies even more readily than albumen and fibrine.

The chemical composition of the albumenoid substances is very complex, and has not been completely elucidated. The composition cannot, therefore, be expressed by a rational formala. Mr. Hunt describes these substances as compounds of carbohydrates (cellulose, sugar, &c.), with ammonia, less the elements of water. Messrs. Dusart, Schoonbrodt, P. Thénard, P. Schutzenberger, and Guignet have obtained artificially nitrogenous substances, which in many of their characteristics are similar to the nitrogenous substances belonging to the animal bodies. This was effected by causing ammonia to act upon sugar, cellulose, and similar substances at a temperature of 150° in sealed tubes. Those substances often designated as epidermic, and also silk, a secreted matter, and the chondrogen tissues, behave in many respects similarly to the albumenoid substances as regards the reactions with heat, alkalies, oxidising agents, nitric and hydrochloric acids, and nitrate of mercury.

Albumen.

Albumen is met with in the animal as well as in the vegetable kingdom; in the former it is found in its normal state, and in solution, in the serum of blood, in the chyle and lymph, in all parenchymatous fluids, in muscle and brain; while the eggs of birds, the ova of reptiles and of fishes are composed chiefly of albumen. The albumen in nearly all these substances is combined with a larger or smaller quantity of an alkali, generally soda. Vegetable albumen is not essentially different from that which occurs in the animal kingdom. The sap of all plants contains albumen, which occurs also in most leguminous seeds, and largely in the fluids known as latex and cambium. All albuminous fluids from the vegetable kingdom exhibit in fresh state an

acid reaction. Albumen as it occurs in the organic bodies of animals and plants is soluble in water; but under the combined action of heat and water albumen becomes entirely insoluble without any perceptible alteration in composition. This very characteristic molecular change is termed coagulation, and is one of the most important properties of albumen. Pure albumen, entirely deprived of the salts and alkalies, which in the natural state accompany it, begins to coagulate at 59.5° C., the change being indicated by a slight turbidity. The turbidity increases with the temperature up to 63° C., when the formation of a flocculent mass commences, complete solidification ensuing at 75° C.

The native solutions of albumen—for instance, white of egg—contain about 1.5 per cent of soda. These solutions do not on coagulation form a flocculent mass, but become gelatinous; the coagulation is never complete, owing to the fact that a portion of the nitrogenous matter remains soluble under the action of the alkali. If there occur a large excess of alkali coagulation does not take place even at 100° C. The action of carbonated or of caustic alkali upon albumen is precisely similar.

Albumen enters into combination with baryta, strontia, and lime, forming therewith insoluble compounds, which when dry are exceedingly hard. The late Dr. Gerhardt held the view that albumen is a bi-basic acid, white of egg and serum of blood containing the acid albuminate, while the coagulation obtained under excess of potassa represents the neutral salt. M. Lassaigne has shown that there can be produced double salts of albumen (or more correctly albumine, since albumen is albumine plus certain salts and soda), having sodium and copper as bases.

Albumen is coagulated, that is, converted into albumen insoluble in water, by most of the mineral acids, and readily by nitric acid at the ordinary temperature of the air. Pyrophosphoric and normal phosphoric acid, as well as the vegetable acids, do not coagulate albumen. Alkaline salts added to a solution of albumen do not effect any change at the ordinary temperature; but as the quantity of these salts is increased the coagulation of the albumen by heat is retarded. Ferrocyanide of potassium, yellow prussiate of potassa, precipitates in the cold all solutions of albumen after the previous addition of some acetic acid. An excess of acetic acid causes the precipitate to be dissolved. If an excess has been added accidentally, the application of gentle heat will effect the precipitation of the albumen. Bichromate of potassa precipitates albumen in the presence of vegetable acids. Several metallic salts, as sulphate of copper, bichloride of mercury (corrosive sublimate), nitrates of lead and silver, as well as alum, precipitate albumen from solution or from the solution of an alkaline albuminate. But the precipitates thus thrown down are generally soluble in an excess of the precipitant. Concentrated alcohol in excess at once effects the coagulation of albumen; dilute alcoholic solutions have the effect of retarding the coagulation of albumen by heat. Tannic acid, aniline, creosote, carbolic acid, and other organic substances possess the property of coagulating albumen.

Coagulated albumen is a white, opaque substance exhibiting an acid reaction to test-paper. After drying, coagulated albumen becomes yellow, transparent, horn-like, and very brittle; in this state it readily absorbs moisture, being thereby increased in bulk. It is insoluble in cold water, becomes liquefied by

long-continued boiling, and at the same time undergoes considerable modification. Coagulated albumen possesses the property of combining readily with a great many colouring materials, such as fuchsine, aniline violet. purpuramide, and others, forming with them true organic lakes; in this respect albumine is very similar to wool. According to Dr. P. Schützenberger's researches, coagulated albumen can be converted into soluble albumen, and again coagulated by the application of heat: for this purpose coagulated albumen* is dissolved in as small a quantity as possible of a weak solution of caustic potassa. The solution of albuminate of potassa thus obtained (free from other salts) is treated with an excess of acetic acid, the precipitate being submitted to dialysis, and the water frequently changed until it is no longer acid. The water of the interior of the dialyser will, on examination, be found to exhibit a slight opalescence; and under the influence of heat, as well as on addition of nitric and other mineral acids, there appears in this fluid a heavy, flocculent precipitate. This precipitate occurs also on adding the solution either of a neutral salt or a very small quantity of an alkali. But fresh albumen when slightly acidified with acetic acid and subjected to dialysis without previous coagulation, exhibit also these phenomena.

The sources of albumen available industrially are the eggs of birds, especially those of the domesticated Gallinacea, and the serum of blood. It is a matter of regret that no substitute has been found for albumen, because the number of eggs withdrawn from the food market for industrial purposes,

greatly increases the price of this very nutritive commodity.

The albumen employed in printing bears a double utility, serving as a vehicle for the colour, and acting at the same time as a varnish. When superfluous albumen colours are washed off after steaming, none of the albumen is removed, but remains as an integral part of the pigment. This occurs in the case of the so-called pigment colours, but in the fixing upon cotton of colours derived from aniline the albumen is in effect a true mordant, for having a great affinity for aniline its action is similar to that of alumina or iron. Pigment colours are fixed upon the cloth merely by the coagulation of the albumen, which does not enter into combination with the colour, but with the cotton fibre.

Albumen as white of egg is met with in commerce in the dry state, having been submitted to a temperature of 30° to 35° C. upon zinc trays, slightly greased with olive oil to prevent adherence of the albumen to the metal. Eighty-four dozen eggs yield on average 6 litres (1·2 galls.) of white in fluid state, and 4 litres (0·88 gall.) of yolk. After drying 14 per cent of commercial albumen is obtained. The yolk finds many applications, as in the dressing of wash-leather, &c. The albumen obtained from blood has the disadvantage of being dark in colour, and is inapplicable except in few instances.

No satisfactory substitute for albumen has yet been discovered; in Germany glue is sometimes employed, the printed cloth being passed through a solution of alum or an aluminous salt to fix the colour; but neither as to fastness nor brightness of colour can this method be commended. Shellac dissolved in borax, india-rubber dissolved in naphtha, and many other solutions have failed. Drying oils have been used as vehicles for the pigment, but are difficult of application; yet were the investigations of Professor G. J. Mulder

^{*} The albumen employed by Dr. Schützenberger was obtained by Lieberkuhn's process.

on the chemistry of drying oils more generally known, undoubtedly these oils would, in course of time, be extensively substituted for albumen.

Qualitative Testing of Albumen.

Dissolve about 5 grms. of the dried albumen in cold, pure water, in which, if itself is pure, it should be perfectly soluble. Add a few drops of acetic acid and filter the solution. There may remain insoluble, coagulated albumen, caseine, and membranous matter; the caseine may be dissolved by treating the insoluble residue with a weak solution of caustic soda, whence it is again thrown down by acetic acid. The clear filtrate is boiled, the dissolved albumen being coagulated and thrown down as a flocculent precipitate. This precipitate is now removed by filtration, and to the filtrate is added a solution of tannic acid in water in order to precipitate any gelatine which might be present. Alcohol may next be added to precipitate gum and dextrine.

Quantitative Estimation of Albumen.

The only important point is to ascertain the quantity of albumen coagulable by heat, and this may be estimated by dissolving a weighed quantity, say 5 grms., of the sample in water, adding a few drops of acetic acid, filtering if required, and boiling the filtrate for some time. The coagulated albumen may then be collected upon a previously weighed filter, washed with boiling water, again with alcohol and ether, dried at 100° C., and weighed.

If a volumetric method be preferred, the following, by M. Scheurer-Kestner, will be found advantageous:-The solution of the sample is diluted to half a litre. From this 100 c.c. are taken, to which 10 c.c. of sulphuric acid are added. Two standard solutions are required, one containing permanganate of potash, the other protochloride of iron, so diluted that one volume of the iron solution discolours or decomposes exactly one volume of the permanganate solution. The protochloride of iron solution may be obtained by dissolving 2 grms. of pure iron (pianoforte wire) in pure hydrochloric acid, and diluting the solution to a litre. The permanganate solution is adjusted to the iron solution volume for volume. Further, there is required a standard solution of pure albumen containing 10 grms. to the litre. The relation of this solution to the permanganate solution should also be accurately adjusted. According to M. Thierry-Miey, this method gives excellent results within 5 per cent; but the gravimetrical method together with qualitative analysis appears to be better suited to the estimation of the quantity of albumen contained in a given sample.

Caseine, Fibrine, and Gluten.

Caseine is the chief nitrogenised constituent of milk. Milk, containing about 12 per cent of solid matter, 3 per cent of which is caseine, agrees in many of its chemical properties and its elementary composition with albumen. Milk is not a solution; but the chief of its solid constituents are in a state of minute division, and the diversity of its solid constituents greatly aids this mechanical admixture. Caseine, as contained in milk, is combined with soda, forming therewith an albuminate identical with the albuminate obtained when previously coagulated albumen combines with soda.

Some chemists admit the existence of two different kinds of caseine, one of which is considered as capable of solution in water before coagulation. That which is called soluble caseine is always more or less contaminated with alkalies or salts, and attempts made to purify caseine by chemical agents result in rendering the caseine much less soluble. It is generally known that milk is coagulated, that is to say, the caseine it contains in solution becomes, by the aid of a slight excess of alkali, solidified on the addition of rennet or an acid, and also by the formation of lactic acid (during souring of the milk), at the expense of a portion of the sugar of milk, the lactic acid combining with the alkali and causing the precipitation of the caseine.

Legumine, contained in the seeds of plants of the natural order of Leguminosæ, is closely approximate to, but not identical with, caseine.

Caseine finds many useful applications in the arts and industries. Mixed with lime it is employed in decorative painting; it enters into the composition of several kits and mastics; is used for glueing together the boxwood employed for woodcuts; dissolved in a solution of borax it constitutes a highly adhesive glue, which is used in fine joiners' work. A mixture of 6 parts of calcined magnesia and I part of oxide of zinc with sufficient caseine to make a paste yields, after desiccation, a perfectly white and very hard mass, which admits a high polish, and appears somewhat similar to meerschaum.

Under the name of lactarine, caseine is employed as a mordant for fixing pigment colours; for instance, ultramarine. Under certain conditions the results are moderately good, but great care and attention are required. Lactarine is insoluble before use, and has to be dissolved in an alkaline liquid, such as ammonia or borax. The colours prepared with lactarine are liable to decomposition, and a colour that may have worked well in the morning, in the afternoon has been known to have changed either into a solid mass or a curdy conglomerate totally unfit for printing, and not re-convertible into good colour again by any means.

Several varieties of fibrine and gluten are known, but their chemical characteristics do not exhibit great difference. The varieties are:—Fibrine spontaneously separated from venous blood; fibrine from arterial blood; fibrine from muscles; glutine, or Beccaria's gluten after it has been exhausted with boiling alcohol. All these substances are insoluble in water; when boiled in water under pressure in a Papin's digester, they become soluble, but are completely altered in their constitution, do not coagulate, nor gelatinise. In acetic and mineral acids fibrine and gluten increase in bulk, and become transparent and gelatinous. Extremely dilute aqueous solutions of caustic potassa and soda dissolve these substances, and acids precipitate these solutions.

CHAPTER X.

REVIEW OF THE METHOD OF APPLYING ALBUMENOID SUBSTANCES IN THE FIXING OF COLOURS.

THE use of albumenoid substances for the fixing of colours has become so extended, that, notwithstanding the high price, there is a constantly increasing demand for these materials. Their method of action is twofold. In some instances there is a genuine chemical combination between the colouring-matter and the nitrogenous albumenoid compound. When, for instance, aqueous solutions of aniline violet (indisine), and albumen are printed upon cotton, the colour when dry appears very dull and without gloss; also, it is not fixed, but may be removed from the cloth by simply steeping in cold water. After steaming, however, the albumen coagulates, and a true combination is formed between the colouring-matter and the albumen on the one hand and the cotton on the other. In this instance the albumen acts as a true mordant. But where albumen is employed to cause a very finelydivided insoluble powder, as ultramarine, to adhere to cloth, and is next exposed to steam-heat, it serves merely as an adhesive, and its action is purely mechanical. This application of albumen is due originally to M. Blondin de la Glacie're, who, in the year 1820, made the first attempt to fix by means of albumen the brilliant blue colour derived from the lapis lazuli, or native ultramarine. As might have been expected from the exceedingly high price of native ultramarine, which is worth, weight for weight, more than gold, the application remained inutilised for several years, owing as well to the few varieties of pigments. Egg-albumen, as a fixing agent, was introduced into this country in 1847; and among the many pigments applied in this manner may be mentioned—Guignet's green, several ochrous compounds of iron, vermillion, zinc-white, some chrome colours, and vegetable lakes.

Albumen, in other words, white of egg, is best adapted to the practical fixation of colour, and would be unrivalled were it not for its high price, and for the consideration that its employment withdraws from use as animal food an enormous quantity of eggs. The best mode of effecting the solution of the dried commercial albumen is in tepid water, which should not be at a higher temperature than 113° to 122° F. (45° to 50° C.); the albumen should be added gradually, and the solution constantly stirred, to prevent the particles of albumen agglutinising. The water should on no account be added to the dried and powdered albumen. The proportion of dry material to the litre of liquid varies according to the specific use for which it is intended, but 300 grms. to the litre is an average quantity. Since white of egg can never be obtained

quite free from particles of those membranes which line the inside of the shell, the solution of albumen should always be carefully filtered through a fine silk sieve, because the presence of small solid particles in the solution, although they may be so small as to be invisible to the naked eye, causes defects of a serious nature in the printing, viz., the production of dark coloured specks upon the cloth.

Albumen of good quality is recognised by its transparency when in flakes, by its taste being not disagreeable, and the odour free from that of putrefaction; it should dissolve readily in cold water with constant stirring. To prevent frothing, and to render the albumen smooth in working, as well as to prevent putrefaction, various additions are made, the material added being probably not the same in any two places. Ammonia, turpentine, and oil are among the principal agents added, but the quantities must be very small. A solution of white bees'-wax in olive oil is sometimes advantageous; bees'-wax and not Japan-wax should be employed. M. Zeller states that good results are obtained by the addition of a certain quantity of fine olive oil to the dry pigments previously to mixing them with the albumen solution; when, for instance, to 2 kilos. of ultramarine 500 grms. of oil are employed, the colour, after fixing, will be at least 10 per cent deeper; and it follows that a smaller quantity or an inferior quality of material may be used. In technical terms the colour "goes further;" while there is the very considerable advantage that after the dressing of the goods they are much more flexible and much smoother than when oil has not been added. In order to obtain good results in cylinder printing it is frequently necessary to add gum to the albumen colours.

A solution of albumen cannot under ordinary circumstances be expected to be long kept free from putrefaction; and true antiseptics have a coagulative effect. It is therefore usual to employ oil of turpentine, which is added with the twofold view of preventing frothing as well as putrefaction. Hyposulphite of soda has been used, but with no good effect. But arsenite of soda, or arsenious acid, commonly known as white arsenic, in the proportion of τ_{00} th part by weight of the albumen, is not injurious to the colour, and, according to M. C. Kæchlin, a high practical authority, the best preservative of albumen solutions.

The following substitutes for albumen have been proposed:—An ammoniacal solution of shellac for the fixing of ultramarine. Copal first softened in aceton, and then dissolved in essence of lavender; fabrics treated with this substitute may be washed in even boiling water. A solution of caoutchouc in coal-tar oil, petroleum, or Persian naphtha has been successfully employed for fixing ultramarine upon woollen stuffs; the method answered well, but has been abandoned on account of the inflammability of the solution, and primarily on account of the discovery of the aniline colours. A solution of resin in linseed oil has been substituted for albumen, as well as gum sandarach and mastic dissolved in acetic acid, the latter not being employed with such powdered colours as ultramarine.

In order to ascertain whether a colour is fixed with albumen, or with any of its substitutes, the fabric should be momentarily immersed in boiling soapsuds and slightly rubbed: well-fixed albumen pigments withstand this treatment, but where substitutes are employed the colour scales off.

CHAPTER XI.

EPIDERMIC PRODUCTS.

THE products of the epidermis, the hair, nails, horn, wool, the scales of some of the lower animals, skin, feathers, are all, chemically, the same substance, but in a different state of aggregation. They are insoluble in water, alcohol, and acetic acid. Solutions of caustic alkalies cause these substances to increase in bulk at the ordinary temperature of the air, but no real solution takes place; on being boiled with alkaline lyes, solution simultaneously with decomposition sets in, ammonia being evolved. The substances contain from 2 to 3 per cent of sulphur. Submitted to the action of water boiling under pressure, in a Papin's digester, they dissolve with difficulty, yielding solutions which do not gelatinise, a characteristic distinguished from that of the organic tissue of bones, cartilage, and the epidermis. The most interesting of these epidermic products is wool.

Wool.

This is a peculiar filamentous material secreted by the skin of sheep and of some varieties of goats. The use of wool for spinning and weaving is of so high an antiquity that it is impossible to say where and with whom it originated, but wool was undoubtedly in use long before vegetable fibres were employed. The cause of this early application is obvious when we consider that wool possesses fineness, flexibility, and elasticity of fibre not met with in an equal degree in any vegetable fibres. Further, wool is naturally either white, yellow, or brown in colour, and can be more readily bleached, while it assumes dyes more easily than vegetable fibre. The Commissioners appointed to inquire into the best means of preventing the pollution of rivers (Rivers Aire and Calder), say, speaking of the woollen trade:-"This trade is of ancient date in England. The Romans had weaving establishments of woollen cloth at Winchester, where the copious springs from chalk afforded means both for power and for washing and dyeing. The mother of Alfred the Great is recorded to have been skilled in spinning wool. Flemish woollen weavers settled in England about the time of the Norman Conquest, and a continued immigration of woollen weavers from Flanders took place in the reigns of Henry I., Henry III., Edward I. and III. The woollen tissues first spun and woven at Worsted, in Norfolk, about the year 1388, became the staple trade of Norwich. Devonshire manufactured woollens soon after the introduction of the trade into England, and Worcestershire a little later. Friezes were also early manufactured in Wales. In the middle of the 16th century Berkshire took the lead in woollen manufacture. About the middle of the last century the West Riding of Yorkshire became the seat of

WOOL. 83

the worsted and woollen trades. Halifax began to be specially noted for kerseys. From about this date, these trades finding so much water available not only for power, but also for washing, dyeing, scouring, fulling, and all other purposes, the Yorkshire manufacturers and traders were enabled to undersell those of other places. In the West Riding there are upwards of 5000 mills and dye works."

Wool, in the more restricted sense, and excluding such fibres as mohair, alpaca, vicuna, and cashmere, is obtained only from sheep. There are two chief species of sheep, viz., the mountain or highland sheep and the lowland sheep. The native sheep of Germany and Spain, the merino sheep, and the electoral sheep introduced into Saxony from Spain about 1765—called electoral, because one of the Electors of Saxony was the importer—belong to the first variety; to the second belong the sheep found in the lowlands of Western Europe and the Russian Steppes, and in this country. The species are further divided, and named according to the county in which they are reared; thus we have Southdown, Leicester, Cotswold, &c. Wool derived from sheep bred and fed for producing meat is inferior in quality and quantity to that of sheep left to follow their natural instinctive selection of food.

Woollen fibre differs in many respects from that of cotton. Its quality varies not only with the kind or species of sheep from which it has been derived, but also with the part of the body of the animal from which it has been taken. The best wool is that from the shoulders, the lower part of the neck, the back, and sides. The length of the fibre varies from 40 to 180 m.m.; the thickness from $\frac{1}{2\delta}$ to $\frac{1}{6\delta}$ of a m.m. When seen under the microscope with a magnifying power of 300 to 400 diameters, woollen fibres appear as a hollow cylindrical tube with rings or projections in regular order, which in arrangement have been compared to the scales of a fish, and these scales are, in fact, the plates of the epithelium. Several of the peculiar properties of wool are attributable to the scaled plates of the epithelium, such as the felting of wool. the harshness felt by the fingers or lips when a fibre of wool is drawn in one direction but not in the opposite, a property exhibited more strongly by hairs than by wool. In working woollen cloths, they are, as is well known, liable to "run up" or contract in certain dimensions, becoming thicker at the same This action is produced purposely in fulling, accidentally by too roughly handling woollen goods in washing and drying, and is attributable to the construction of the wool fibre, which may be regarded as an arrow or a fish-hook easily moved in one direction, but not capable of returning.

Once a year the wool is shorn from the sheep and washed. By the washing the wool loses 20 to 70 per cent of its weight. The weight of wool thus shorn off varies from 3 to 12 lbs. per head of sheep. We may here again quote from the Commissioners' Report on the Pollution of Rivers. "The object of the washing is to remove ordinary dirt and the natural grease, as well as that which has been applied to the fleece, and to open the wool to the action of the dye. The wool is immersed in a copper filled with stale human urine, diluted with water, and heated by steam. In this bath it remains for a time varying from half an hour to two hours, when it is laid upon a grating placed over the copper to drain, and then removed to another vessel to be washed with cold water. The action of stale urine probably depends upon the presence of free animonia or its carbonate. Pig's dung is

sometimes employed instead of, or in combination with, the urine. Other substances, such as soda-ash, phosphate of soda, and salts of ammonia, are sometimes substituted or added to this bath, but the favourite material seems to be stale human urine. The wool, after being drained, is washed in cold water. In the smaller mills this is performed by stirring up the wool in a tank of water with a strong pole, the water being let off through a "clow" or shuttle, furnished with a grating, at the bottom of the vat, which is again filled with cold water, the water being renewed several times in succession. In late years a machine known as Petrie's wool-washing machine has been introduced. The wool, steeped as before, is here immersed in water contained in long tanks, and is made to pass forwards, being at the same time opened out by an ingenious arrangement of rakes worked by machinery. principle in this case is to introduce the wool to liquid which is already fouled by having passed over a first portion, and so gradually to bring it into contact with clean water at the other end. Three or four of these vessels are placed in series, and the wool transferred from one to the other by endless bands of wire gauze. The wool is put into a tank, from which the waste water flows away, and issues from the tank to which the clean water is supplied. The use of this machine offers an opportunity of economising water, which is of great advantage when the supply is limited. This 'scour' water runs, in either case, from the vats to the nearest outfall. There is nothing in it that is considered worth saving, and we have not heard of its ever having been turned to account or treated in any way. If the wool is not to be dyed, or is to be removed from the premises for that purpose, or if it is to be woven before being dyed, it is dried in hot chambers of various constructions."

The following analysis of raw merino wool, by M. Chevreul, exhibits the composition after drying at 100°. In 100 parts by weight—

Earthy matter deposited by washing the wool in water									
Suint, a peculiar saponified grease, soluble in cold water 3	2.74								
Neutral fats	8.57								
Earthy matters obtained after the fatty substances were elimi-									
nated	1.40								
Textile fibre	1.53								

Faist gives the following analysis of various wools:

		(ra	im Wool	Hohenheim (washed and dried).	Hungarian Wool (washed and dried).
Mineral matter			16.8	0.04	1.0
Suint and fatty matt	er 4	4.3	44.7	21.00	27.0
Pure wool	3	8.0	28.2	72.00	64.8
Moisture	1	1'4	7.0	6.06	7.2
	No.				
	IC	0.0	100.0	100.00	100.00

Elsner has found that the loss of weight in wool, treated for the elimination of the suint with bisulphide of carbon, varies from 15 to 70 per cent with washed merino wool, 50 to 80 per cent with unwashed wool, and with long or carded wool 18 per cent.

Suint contains oxalate of lime, chloride of potassium, silica, valerianic acid, two potash salts containing peculiar fatty acids and some fats none of which

WOOL. 85

are found in the body of the sheep in that peculiar state. The fibre itself, after having been treated with water, alcohol, and ether, still contains o'a to o's per cent of ash, composed of phosphate of lime and magnesia, sulphate and carbonate of lime, silica, and peroxide of iron. The organic substance of the fibre, often called keratine, consists of a proteinoid substance, containing or combined with large quantities of sulphur, a considerable proportion of which is readily removed by the action of alkalies. When wool is steeped in plumbite of soda—a solution of oxide of lead in caustic soda—the fibre becomes coloured black, owing to the formation of sulphide of lead, due to the sulphur naturally contained in the wool. At 150° F. wool gives off sulphurous odours; even during the boiling of wool and woollen fabrics in water -flannel, for instance-an odour of sulphur is perceptible. Hence it follows that, in dyeing wool with bright colours, contact with metallic surfaces, and the presence of salts of lead, copper, and tin must be carefully avoided. Especially is this the case with steam-colours. The intelligent Directeur de la Manufacture des Gobelins, at Paris, eliminates the sulphur from the wool used in that establishment by soaking the wool for twenty-four hours in milk of lime, at the ordinary temperature of the air, and then washing the wool in dilute hydrochloric acid, and afterwards in water. It appears, however, that even when this treatment is repeated twenty-eight times, for forty-eight hours each time, all the sulphur will not have been eliminated, and there may even then remain 0.46 per cent of sulphur; but the wool is no longer coloured by contact with plumbite of soda.

Wool deprived of naturally-adhering grease, and heated to 160°, assumes a yellow tinge, which is deeper when the wool has previously been de-sulphured. If the wool has not been deprived of the grease adhering to it naturally, it becomes, when heated to 160°, coloured brown. Heated to 130° wool gives off ammonia, and, similarly to most protein compounds, wool does not admit of being heated beyond 120°, in a current of dry air, without suffering decomposition. Schweitzer's reagent does not act upon wool at the ordinary temperature of the air, but it dissolves wool when heat is applied. Chlorine and hyperchlorous acid attack wool at the ordinary temperature, causing it to assume a yellow colour; hence wool and woollen fabrics cannot be bleached by chlorine. Nitric acid, even when dilute, colours wool yellow, forming xanthoproteic acid: this property is sometimes utilised in the printing of patterns upon woollen fabrics, especially such as have previously been dyed blue with indigo, for the nitric acid, in destroying the indigo, gives a deeper shade of yellow. Caustic alkalies disintegrate and dissolve wool very rapidly; strong ammonia acts injuriously upon wool, causing it to become rapidly disintegrated. The solutions of the alkaline carbonates and of soaps, if not too concentrated, and if at a lower temperature than 60°, do not perceptibly affect wool and its tissues.

When wool is ignited it burns slowly, emitting a very disagreeable odour, similar to that given off by burning horn. A woollen thread held in the flame of a candle leaves a voluminous coke, which remains hanging at the end of the thread. This property is often employed in the detection of woollen fibre.

Wool, especially when roughly washed and purified, is very hygroscopic, and though dry to the touch may have absorbed between 7 and 8 per cent of moisture. The behaviour of wool towards colouring matters and dyes is

entirely different from that of vegetable fibres. It forms, with some soluble colouring materials, genuine compounds or lakes, and acts generally in this respect as do all protein substances. Several salts, including alum, are precipitated by wool from their aqueous solutions, and retained in the wool by a special attractive force. Wool has the property, also, of reducing the peroxides of some of the metals, including iron, to protoxides.

Before wool is ready for the spinner it has to undergo, as already described, a process of washing, in order to remove the dirt accidentally adhering to it, and to eliminate that natural grease which protects the animal from the chills which would be consequent upon the thorough saturation of its coat with rain. As this grease has been found to contain a large quantity of a very pure carbonate of potassa, Messrs. Maumené and Rogelot have devised a method of extracting the potassa-salt, so as to obtain from every 1000 kilos. of wool about 75 kilos. of the carbonate. The method consists in steeping the wool in tepid water (35° to 40°), employing repeatedly the same liquid, and maintaining the heat by the occasional admission of steam when fresh quantities of wool are put into the tanks, or rather tubs, wooden vessels being employed. The liquid, when as much saturated with saline matter as possible, is run off, evaporated to dryness, and the residue ignited. The complete elimination of fatty matter from the wool is effected by washing in weak alkaline liquids, partly composed of putrid human urine (carbonate of soda), partly of carbonate of soda.

Bleaching Wool.

The bleaching of woven woollen tissues, or also of woollen yarn (a large proportion of the wool employed is dyed before weaving), includes numerous operations, some of which are of a mechanical nature, as, for instance, the firing or removal by singeing, or in some cases by shaving or shearing off, the loose, downy threads. The woollen fabric is never dyed with the view of preserving any part of it white, because affinity of the fibre for colours is so great that it takes them without any mordant, and whites therefore could not be kept clear in dyeing. For this reason, also, the loose hairs on the cloth may be shaven to any degree of closeness.

The bleaching of wool is not a matter of great difficulty, and is far less laborious than the bleaching of cotton and linen. From the chemical nature of the wool it will be gathered that it is impossible to apply to it materials of the same strength and temperature as are applied to cotton and linen. The process of bleaching wool is a repetition of gentle treatment with soap and very weak alkalies (carbonates); but when the woollen fabric is required to be dyed with light or bright colours, or is to be printed, the ground must be white, and the process of sulphuring resorted to. This was formerly effected by hanging the moist pieces for several hours in chambers filled with sulphurous acid gas, or vapours of burning brimstone. It is now performed by Mr. Thom's process, in a few minutes, by passing the goods over a number of rollers confined in a small chamber filled with the same vapours. According to Mr. Girardin (a great authority in all matters relative to bleaching, dyeing, &c.), M. Pion, at Elbeuf, the seat of an extensive woollen industry in France, obtains excellent results by employing a solution of sulphite of soda acidified with hydrochloric acid, in which the woollen tissues are steeped for some hours, being next thoroughly washed, - an operation equally indispensable after

sulphuring with gas, because there is generated in the fabric a small quantity of sulphuric acid, which, unless removed by washing, would during the drying tend to destroy the fibre. Woollen fabrics intended to be dyed with dark colours are never bleached by sulphuring. Cloth intended to remain white is, after the sulphuring and washing, passed through a bath containing some indigo-carmine, in order to increase the intensity of the whites. According to M. Schlumberger, skeins of woollen thread can be excellently bleached by washing them thoroughly in a strong soap solution, at a temperature of 50°, and suspending them wet during the night in a chamber filled with sulphurous acid gas. The skeins are then dried, without being again rinsed. When the wool is intended to be dyed it is put, immediately after being taken from the sulphuring room, into a bath of dilute sulphuric acid, and next thoroughly washed in cold water.

CHAPTER XII.

PRACTICAL RECIPES IN CONNECTION WITH WOOLLEN YARN AND FABRICS.

Bleaching.

N quantities of 100 lbs. The process is very simple. The scourer should have care that his kettle is not hotter than 132° F., and that the wool does not lie in the bath long enough to become yellow. The goods or yarn are scoured in clean soap, as usual, and then hung up in a closed chamber or bleach-house, exposed to the vapour of sulphurous acid, produced by burning in an iron pot 6 or more pounds of brimstone. When yarn is bleached for the market, it should be put into the sulphur-house without the soap being rinsed out, only switched out well. If the white has to be coloured, the wool should first be run through a cold bath, containing 2 lbs. of muriate of tin, 2 ozs. of extract of indigo, 3 ozs. of cochineal paste.* Red, blue, and yellow form white, and the wool is naturally yellow; hence the method of treatment. Then take the wool into the sulphur-house. The fabric ought never to be coloured after sulphuring, as it will become spotted. Carpet-yarn may be afterwards run through a bath containing 5 lbs. of whiting: this somewhat neutralises the offensive odour. Care should be taken in bleaching part cotton goods when poles or slats are employed; the wood absorbs sulphuric acid, and will rot the cotton if in contact with the cloth. The poles should be often washed or planed.

Another Method of Bleaching.

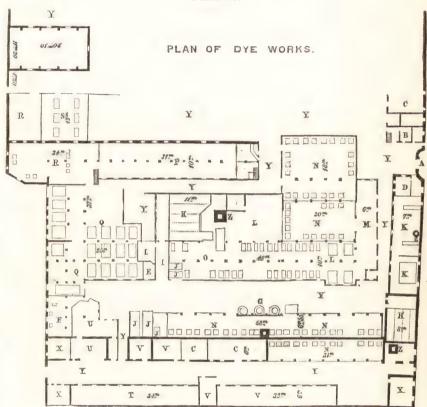
In the case of a large quantity of goods for printing, it is more convenient to bleach them in large vats filled with water, charged with sulphurous acid, as follows:—

Half fill a stone pot with pine sawdust, and cover it with a wooden cover through which is a hole to receive a lead or glass pipe. Pour enough sulphuric acid to cover the sawdust, and insert the pipe which conducts the sulphurous acid gas into the vat of water, rendering the joint gas-tight by a luting of clay. To prevent too much free acid going over, the gas may be passed through a strong solution of soda, and then to the vat. The vat, of course, should be covered. The goods are thrown into the water over-night, and when taken out will be found sufficiently bleached.

This method, when modified, will be found advantageous in bleaching the whites of goods coloured chrome-black, should such a process be required.

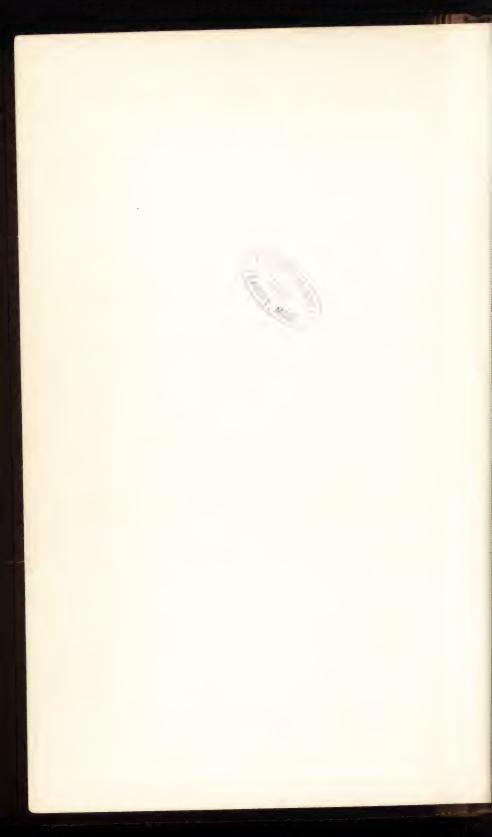
^{*} Cochineal paste is obtained by placing 10 lbs. of Honduras cochineal in a vessel, and adding 30 lbs. of ammonia water (17° B.), stirring the mixture well. The vessel should be covered with a cloth, and allowed to stand for a few days. The vessel is then to be immersed in boiling water, in order to evaporate the superfluous ammonia; when the evaporation is complete the mixture is ready to be used. The ammonia may be condensed during the evaporation, if employed in large quantities.

Plate II.



PLAN OF THE DYE WORKS OF BOUTAREL AND CO., CLICHY-LA-GARENNE.

A, Entrance. B, Lodge. c, Warehouse, Offices on the first floor. D, Chemical Laboratory. E, Mill for Chipping Dye-woods. P, Mill for Wares. G, Boilers for Extracting Dye-woods. H, Steam-boilers. I, Engine-house. J, Water Tanks. K, Singeing-house. L, Crabbing-house. M, Dye-houses. O, Washing and Drying. P, Stretching Pieces on first floor, Examination of Pieces. Q, Croppers in the first floor, Finishers on the ground floor. R, Pressing-house. S, Trimmers. T, Shawl-house. U, Mechanics' Shop. V, Store of Materials. X, Lodgings of Persons employed. Y, Yards and Passages. Z, Chimney.



To each piece of fabric dissolve I lb. of hyposulphite of soda in 2 pails of water, to which add I lb. of sulphuric acid, the vessel containing the mixture being well covered, so as not to lose any sulphurous acid gas. All the sulphur must be allowed to settle until the liquid is clear, and the liquid may then be run into a clean tub filled with water. In this bath the goods are to be laid for 6 to 8 hours, when the whites will be found perfectly bleached without injury to the black. Rinse, and dry.

COLOURS ON WOOLLENS-BLUES. Woad.

Woad alone was used for colouring wool blue before indigo was introduced into Europe. The introduction of indigo was a great advantage to the dyer, not only for its intrinsic value, but because he could daily strengthen his vat, using the old woad as a fermenting agent, like yeast in making bread. As to the practical value of the different varieties of indigo, it may be said that 4 lbs. of good Bengal are equivalent to 5 lbs. of good Guatemala indigo.

In order to colour with indigo we have to deprive it of its oxygen, The deoxidised indigo is yellow, and in this state penetrates the woollen fibre; the more perfectly the indigo in a vat is deoxidised, the brighter and faster will be the colour.

To a vat 8 feet deep by 6 feet wide, filled with water, and heated by steam or otherwise to 140° F., add 200 lbs. of woad, about 10 lbs of well-ground indigo,or more, according to the amount of work to be done, -5 lbs. of soda, & a bushel of good wheat-bran, 10 lbs. of good madder, and 1 lb. of flour. If the soda, bran, madder, and flour are boiled for five minutes before adding them to the vat, it will ferment twelve hours earlier than it would otherwise do. Stir the vat well, and after eight hours' rest again stir. The vat by this time should have commenced to ferment, the liquid acquiring a mottled appearance. When the fermentation is well established, add about 2 lbs. of slaked lime, and again stir. If sufficient lime has been added, the surface of the vat will reflect a golden colour; and a sample of wool immersed in the liquid for about twenty minutes should become perfectly coloured blue in one minute. A green colour remaining with the wool after one minute shows that more lime must be added. Should this addition be neglected, the vat will be, as it is termed technically, "lost." The lime added should be mixed with water, and the solution filtered. A vat, to which too much lime has been added, or which has become "over-sharpened," acquires a brown colour, and the wool immersed in the liquor is imperfectly coloured a grey-blue. 2 or 3 lbs. of sulphuric acid may be added in such a case to form with the lime a neutral sulphate, which settles to the bottom of the vat. After the addition of the sulphuric acid a mixture of 5 lbs. of bran and 5 lbs. of madder boiled together should be added. Fermentation is thus again set up, and can be reduced by lime as before. When the vat is exhausted; and more indigo must be added, care should be taken that the liquor is sharp enough. The liquor should again be warmed, and the indigo added with about 6 lbs. of madder, 6 lbs. of bran, and 2 lbs. of soda, boiled together as before. The indigo should be added over-night, in order that fermentation may be complete by the morning. In the morning lime must be added until the golden film forms on the surface of the liquid.

Soda or Potash Vat.

By boiling 10 lbs. of indigo in a solution of 4 lbs. of caustic soda or potash, and adding 2 lbs. of feathered tin, or 3 lbs. of tin crystals, the indigo is deoxidised by the strong affinity of the tin for the oxygen. The ordinary method of fermentation is, however, to be preferred, as a larger quantity of work can be got through. But the soda vat is preferable for light blues, as a brighter colour is obtained than by the woad vat, while larger quantities of goods may be coloured more easily. Potash should be employed for linen and cotton.

A Decomposed Vat.

A decomposed, or, as it is termed, a "sick" or "green" vat may be known by its dark colour and freedom from odour, and more certainly by the addition of lime, bran, madder, and soda, or of woad. If, after several hours, the vat is restored, it may be worked with care as a new vat.

Applications of the Woad Vat.

The applications of the woad vat, as well as many practical recipes relating to the colouring of wool, we shall, for facility of reference, include in this chapter.

Indigo-Blue on Wool for Topped Hosiery.

roo lbs. of wool are coloured with 4 lbs. of Guatemala or 3 lbs. of Bengal indigo, in the woad or soda vat. There is then prepared by boiling for a few minutes 5 lbs. of cudbear or 8 lbs. of orchil paste, adding to the mixture 1 lb. of soda, or an equivalent quantity (about one pail) of urine. The beck must be cooled to 170° F. before the wool can be entered. It should be handled for twenty minutes, taken out, rinsed, and dried. 3 ozs. of aniline purple dissolved in half a pint of alcohol can be used instead of the cudbear. The shade produced is very pretty, but ought never to be used for mixed goods, which have to be bleached, as it runs into whites. The cudbear, too, is affected by sulphuring.

Dark Blue, for Wool for Broadcloth.

A healthy woad vat is employed for this colour. The wool is handled slowly for one hour, then removed; after two hours it can be again dipped until it has acquired the desired shade. Enough indigo should be added to the vat to colour the wool in three immersions; that is, about 10 lbs. of good indigo to 100 lbs. of wool. The wool may with advantage be taken through a warm bath containing 2 lbs. of sulphate of copper; this additional immersion renders the colour faster in fulling. A dark blue, very common in the market, is topped with camwood or red sanders, the latter being boiled on the coloured wool.

Topped Logwood Blue.

Dip in the blue vat and then rinse. Boil the wool thus dipped for one hour in a kettle containing 10 lbs. of alum, 2 lbs. of crude tartar, and 1½ lbs. of sulphate of copper. Remove and cool. To some fresh water add 5 to 10 lbs. of logwood (according to the shade required, and the quality of the logwood) in a bag. Boil, and then cool the kettle to 170° F. The wool may now be entered and handled slowly; in one hour it may be cooled, rinsed, and switched for drying.

Indigo-Blue, part Logwood.

For 100 lbs. of cloth. Colour the cloth in the indigo-blue vat, and rinse well. Then boil the cloth in a bath of 20 lbs. of alum, 2 lbs. of tartar, 5 lbs. of pensée mordant or purple acid,* for two hours. Remove and cool. To a kettle of fresh water add 10 lbs. of logwood in a bag, boiling for half an hour. Cool to 170° F., and enter the wool, boiling half an hour. Cool and rinse.

Purple Blue.

For 100 lbs. of wool. The wool is first coloured lightly in the blue vat. It is then boiled in a solution of 15 lbs. of alum and 3 lbs. of tartar for one and a half hours. Remove, cool, and drain for twenty-four hours. In a kettle of fresh water boil 8 lbs. of cochineal powder for ten minutes. Cool to 170°, and enter the wool for one hour; boil for three quarters of an hour, rinse, and dry.

Chrome Blue.

For 100 lbs. of wool. Boil the wool for one hour in a solution of 3 lbs. of bichromate of potash, 6 lbs. of alum, 1 lb. of tartar. Remove, cool, and rinse. In a kettle of fresh water boil 6 lbs. of logwood for half an hour, add 3 lbs. of dissolved cudbear. Cool to 180° F., and enter the wool, boiling and handling for three quarters of an hour. As chrome colours always darken in drying, the shade, on removal from the bath, must be lighter than that desired in the finished fabric.

Dark Indigo Blue.

For 100 lbs. of cloth. Boil for one hour and a half in a solution of 20 lbs. of alum, 4 lbs. of tartar, 6 lbs. of pensée mordant, 6 lbs. of extract of indigo. Remove and cool. Prepare a fresh kettle of 8 to 10 lbs. of logwood, in which boil the fabric for one hour.

Saxony Blue.

For 100 lbs. of thibet or combed yarn. Dissolve 20 lbs. of alum, 3 lbs. of tartar, 2 lbs. of pensée mordant, 3 lbs. of extract of indigo, or, better, 1 lb. of carmine, in hot water. Cool to 180° F.; enter the material, and boil until the colour becomes even. Too long boiling should be obviated by well and quickly handling.

It is necessary to handle coarse carpet-yarn through a beck heated to 170° F., and containing 15 lbs. of alum, 10 lbs. of sulphuric acid, 4 lbs. of chemic paste or sulphate of indigo. Under the influence of sulphur the colour becomes of a stone-green shade, but is restored by rinsing in water.

Fast Prussian Blue.

For 100 lbs. of wool or flannel. Dissolve 8 lbs. of red prussiate of potash (ferricyanide of potassium), 2 lbs. of tartaric acid, 2 lbs. of oxalic acid, and the following mordant in water heated to 208° F., in which the goods are to

* This mordant can be prepared by mixing in a stone vessel 5 lbs. of tartar, 5 lbs. of feathered tin, with 25 lbs. of muriatic acid. To this mixture is added 15 lbs. of sulphuric acid diluted with 10 lbs. of water; then very slowly 2 lbs. of nitric acid.

+ Sulphate of indigo may be roughly prepared thus:—To 30 lbs. of sulphuric acid (67° B.), add slowly 10 lbs. of pulverised fine Bengal indigo. Stir until all is well mixed. After two days add slowly 10 lbs. of water.

be well handled for one and a half hours. Then remove, allow to drain, rinse, and dry.

The mordant. Add x lb. of feathered tin to 10 lbs. of nitric acid (36° B.), 10 lbs. of hydrochloric acid (22° B.), 10 lbs. of sulphuric acid (66° B.), diluted with water.

Some dyers themselves prepare the red prussiate of potash by passing chlorine (obtained by the action of sulphuric acid upon manganese and salt) through a leaden pipe into a solution of yellow prussiate of potash. A dark olive liquid is produced, which yields on evaporation crystals of red prussiate. When nitrate of iron no longer produces a blue colouration enough chlorine has been taken up. The olive liquid can be employed without crystallisation.

Aniline Blue.

For 100 lbs. of fabric. Dissolve 1½ lbs. of aniline blue in 3 quarts of boiling alcohol. Filter the solution, and add the clear filtrate to a bath of water at 130° F., together with 10 lbs. of sulphate of soda, and 5 lbs. of acetic acid. The goods are now to be entered and handled for twenty minutes, when the temperature of the bath is to be slowly raised to 200° F. At this temperature add 5 lbs. of sulphuric acid diluted with water, Boil for twenty minutes, rinse, and dry. The aniline blue should be added in two or three quantities in order to render the colouring of equal quality throughout. Closely woven fabrics, braid, &c., should be prepared in a boiling solution of 10 lbs. of sulphuric acid and 2 lbs. of tartaric acid before colouring with the aniline.

REDS ON WOOL.

Scarlet.

For 100 lbs. of fabric. Boil for fifteen minutes 11 lbs. of Honduras cochineal, 5 lbs. of tartar, or 3 lbs. of tartaric acid, 2 lbs. of oxalic acid, 1 lb. of tin crystals, 1½ lbs. of flavine, 10 lbs. of muriate of tin (see footnote, p. 91) Cool to 180° F., and enter the goods, boiling for one hour. Remove, cool, and rinse. 5 lbs. of hydrochloric acid added to the beck will prevent the appearance of undyed filaments of wool, &c. This addition is attended with good results in all kinds of scarlets, orange, and pinks.

Scarlet (Lac-Dye).

For 100 lbs. of flannel or yarn. Boil in water for fifteen minutes 25 lbs. of lac-dye, 15 lbs. of muriate of tin, 5 lbs. of tartar, 1 lb. of flavine (the quantity of which may be varied according to shade), 1 lb. of tin crystals, 5 lbs. of hydrochloric acid. Cool to 170° F., and enter the goods, boiling for one hour. Rinse whilst hot. This is a faster colour than

Cochineal Scarlet.

For 100 lbs. of fabric. Dissolve in water 10 lbs. of nitrate of tin, 5 lbs. of cream of tartar, and 1 lb. of flavine. Boil the solution for ten minutes, and cool to 170° F. Enter the goods, boiling for one hour. Remove, cool, and rinse.

To a kettle of fresh water add 7 lbs. of cochineal and 2 lbs. of starch in solution. Strain, and then boil for five minutes. Cool to 180°, and then add

1 lb. of nitrate of tin. Enter the fabric and boil for three quarters of an hour. Remove, cool, and rinse.

Ponceau.

For 100 lbs. of fabric. Colour scarlet, as for scarlet dyeing, but without flavine or yellow dye-stuff. Then well rinse the goods. Prepare a kettle of fresh water heated to 180°, into which put 5 lbs. of cochineal paste (see p. 88). Stir, and enter the fabric without boiling. Rinse and dry. Magenta crystals may be substituted for the cochineal.

Pink for Listings.

For 100 lbs. of wool. Boil together, until dissolved, 8 lbs. of cochineal, 5 lbs. of tartar, 10 lbs. of muriate of tin, ½ lb. of tin crystals. Cool to 170° F., and enter the wool, boiling for half an hour. Should the wool not colour evenly add a few lbs. of hydrochloric acid. If the listings are to be on white flannels, add about 6 lbs. more of muriate of tin to the beck before removing the wool. To prevent the colour running the scourer should add a solution of 1 lb. of hydrochloric acid to the last rinsing of the flannel. Should the cochineal have been smeared upon the white it should be well rinsed out with cold water before sulphuring.

Madder Red.

For 100 lbs. of fabric (generally cloth for army uniforms). Dissolve 20 lbs. of alum, 5 lbs. of tartar, 5 lbs. of muriate of tin. Enter the goods, boiling for two hours. Remove, cool, and drain over night. Into fresh water stir 75 lbs. of good Dutch madder. Enter the fabric at 120° F., and raise the temperature to 200° in one hour. Handle, rinse, and dry.

Magenta.

For 100 lbs. of fabric. Dissolve 8 ozs. of magenta crystals in boiling water and strain through a flannel sieve. Cool the bath to 170° F., in which handle the fabric half an hour. Varying the quantity of magenta crystals will cause variation in the shade. A few lbs. of soap will aid in securing evenness of colour.

Crimson with Cochineal.

For 100 lbs. of thibets. Dissolve 10 lbs. of tartar, 6 lbs. of nitrate of tin, and boil the goods in this solution for two hours. Prepare a fresh bath with 20 lbs. of cochineal paste with water at 170° F.; increase the temperature to 200°. Remove, cool, and rinse.

Where hard water is employed the colour will be very brilliant; in the case of river water about 3 lbs. of whiting may be added. For Orleans with Turkey red warps the colouring should be effected in one operation, the paste, tartar, and nitrate of tin being all added at once. Muriate of tin must not be employed.

Rose-Pink.

For 100 lbs. of fabric. Dissolve 5 lbs. of alum, 5 lbs. of cream of tartar, 2 lbs. of saleratus, 5 lbs. of muriate of tin, with sufficient cochineal paste to produce the required shade. Handle the fabric at 180°F. This colour is faster and better suited for carpetings than that obtained with magenta.

Dahlia.

For 100 lbs. of wool. Stir 20 lbs. of good cudbear in a little water, straining through a sieve into a clean kettle. Heat the bath to 180°, and then add 2 lbs, of muriate of tin. Enter for one hour without boiling. Rinse and dry.

Crude acetic acid or wood vinegar can be used to obtain fine red shades of peach colour, and ammonia or pearl-ash for blue shades. Orchil may be substituted for cudbear. This dye should never be boiled.

Maroon.

For 100 lbs. of wool. Boil 20 lbs. of cudbear, or 25 lbs. of orchil, and 4 ozs. of magenta crystals for ten mintes. Cool the dye to 175° F. Enter the fabric or wool, increase the temperature to 212°. Remove, rinse, and dry.

YELLOWS.

Yellow.

For 100 lbs. of wool. Dissolve 15 lbs. of alum, 4 lbs. of cream of tartar, 10 lbs. of muriate of tin, 1 lb. of tin crystals, 2 lbs. of flavine, or 8 lbs. of quercitron bark. Boil until the flavine is dissolved, and cool to 170° F. Enter the wool, and while handling raise the temperature to 212°, then allowing the goods to remain for three quarters of an hour. Remove, cool, and rinse. Cochineal may be added for dark yellows, omitting the alum if the colour approaches orange, as it causes this colour to become dull and blurred. A few pounds of sulphuric acid will sometimes increase the brilliancy of the yellow. Picric acid is employed for delicate tints of yellow, and may be made fast by muriate of tin.

Balge Yellow.

This colour is generally employed on cassimere for vestings. The goods should be previously well bleached by sulphuring.

For five pieces of goods each of 10 lbs. weight. Dissolve in water, heated to 140° F., 5 lbs. of alum, 2 lbs. of muriate of tin, and the liquor from 3 lbs. of fustic. The tannic acid should be previously eliminated from the fustic by adding ½ lb. of glue to the boiling fustic liquor. Handle the goods until the required shade is obtained.

Orange.

For 100 lbs. of wool. Boil for ten minutes 5 lbs. of tartar, 3 lbs. of flavine, 5 lbs. of cochineal, 1 lb. of tin crystals, 10 lbs. of muriate of tin. Cool the kettle to 180° F., and enter the wool for ten minutes. Then if even boil for half an hour; if uneven, add 8 lbs. of hydrochloric acid. Rinse and dry.

Salmon.

For 100 lbs. of wool. Boil for ten minutes 10 lbs. of alum, 3 lbs. of tartar, 1 oz. of flavine, 5 ozs. of cochineal, 6 lbs. of muriate of tin, 2 lbs. of hydrochloric acid. Cool to 180° F. Enter the wool, handle, and boil until even. Cool and rinse. The shade may be varied by adding more or less cochineal or flavine.

Salmon with Madder.

For 100 lbs. of wool. Dissolve 10 lbs. of alum, 3 lbs. of tartar, 4 lbs. of muriate of tin, 3 lbs. of madder, 4 lbs. of hydrochloric acid. Heat to 170° F.,

and enter the goods for half an hour, during which time increase the temperature to 212°. The madder being a fast colour, the wool must be handled quickly at first, because longer boiling will not remove patches.

GREENS.

Green for Broadcloth.

For 100 lbs. of wool. Dissolve 15 lbs. of alum, 3 lbs. of tartar, 3 lbs. of muriate of tin, and 20 lbs. of fustic. The fustic should, of course, be first boiled in water, to which the other constituents of the kettle may be added. The wool should be entered, and the dye raised to slow boiling for about one hour. Remove and cool. Prepare with fresh boiling water 30 lbs. of weld as a bath, to which add 3 lbs. of soda. Cool to 180° F., and enter the prepared wool, allowing it to remain for one hour; but the bath must not be brought to the boil. Remove. The wool is now coloured a fine yellow, and is finished with indigo in the blue vat.

This mode of colouring is expensive, but the results are good.

Another Green for Broadcloth.

For 100 lbs. of wool. Colour well in the blue vat. Dissolve 15 lbs. of alum, 2 lbs. of tartar, 2 lbs. of sulphate of copper, in which bath boil the wool for one hour. Prepare a fresh kettle by boiling 25 lbs. of fustic and 8 lbs. of logwood in water. Cool to 180° F., and enter the prepared wool, handling well for ten minutes; then increase the temperature to 212° for half an hour. Remove and cool. The colour may be tested by hand-fulling with strong soap.

Logwood Green.

This colour is a common one, better suited to coarse cloth. For 100 lbs. of broadcloth. Boil the cloth for one hour in a solution of 15 lbs. of alum, 3 lbs. of tartar, 2 lbs. of sulphate of copper. Remove and cool. Boil in fresh water for half an hour 15 lbs. of fustic and 10 lbs. of logwood, into which bath, at a temperature of 180°, reel the cloth for one hour, and then expose it to the air. During the airing run off half the liquor, and reduce the temperature to 130°. Then add the solution of 2 lbs. of pearl-ash, or of 3 lbs. of soda-ash or 4 pails of urine. Reel the cloth for twenty minutes and wash. If darker shades should be desired, more logwood may be employed.

Chrome Green.

For 100 lbs. of wool. Dissolve 4 lbs. of bichromate of potash, 10 lbs. of alum, and 2 lbs. of tartar in a kettle of fresh water, in which boil the wool for one hour. Remove, cool, and rinse. Prepare an infusion of 20 lbs. of fustic and 10 lbs. of logwood. Cool to 180°, and enter the prepared wool, boiling for half an hour. Cool, and rinse. This colour darkens in drying and finishing, and is not very durable.

Green for Yarn.

For 100 lbs. of yarn. Dissolve by boiling 20 lbs. of alum, 8 lbs. of sulphuric acid, 3 lbs. of extract of indigo, 1 lb. of picric acid. Cool to 180° F., and enter the yarn, bringing the bath, after quickly handling the wool, to a boil. The

addition of a few pounds of common salt will assist in rendering the colour even, especially if the yarn be spun of new wool.

Aniline Green.

The crystals of aniline green are red-coloured in dry state; the colour is not so brilliant from aniline crystals that have been kept even a short period of time. The dye is, therefore, best prepared immediately before use; and the following method may be adopted, as recommended by Dr. Reimann ("Handbook of Aniline Colours," pp. 77 to 133). 3 lbs. of magenta crystals are mixed with 3 lbs. of sulphuric acid and 1 lb. of water. To this solution, when cold, 1½ lbs. of aldehyde are added, and the whole well mixed upon a water-bath until the liquid, when dropped into acidulated water, exhibits a fine blue colour. The solution may then be poured into 8 gallons of boiling water, to which is added the solution of 3 lbs. of hyposulphite of soda. Boil this liquid for a few minutes, and filter through a cotton cloth. A fine green dye passes through the filter as the filtrate, and a dark blue-gray residue remains. Coloured silk with aniline green, when exposed to 300° of dry heat, changes to blue, but coloured wool suffers no change.

Aniline Green with Picric Acid.

For 100 lbs. of woollen goods. First colour with aniline blue, as described under Blue. Remove the cloth or yarn, and add 1 lb. of picric acid and 6 lbs. of alum to the dye. When the solution is complete, enter the woollens, boil for twenty minutes, cool, and rinse. This green is not so fast nor so bright as the former.

Olive-Green.

This colour is chiefly used for broadcloths. For 100 lbs. of wool. Dip first in the blue vat. Then prepare a kettle by boiling 20 lbs. of fustic and 10 lbs. of logwood; to the infusion add 10 lbs. of alum, 2 lbs. of tartar, 2 lbs. of sulphate of copper, 10 lbs. of madder, 10 lbs. of turmeric. Boil for ten minutes, and then cool the dye to 180° F. Enter the blued wool, handling well for ten minutes, and boiling for one hour and a half. The shade may be varied by the addition of more or less logwood or madder.

OLIVES.

Bichrome Olive.

For 100 lbs. of wool. Boil the wool for one hour in a kettle in which has been dissolved 2 lbs. of bichromate of potash, 2 lbs. of tartar, and 5 lbs. of alum. Remove, cool, and rinse. Prepare by boiling for ten minutes a kettle of 20 lbs. of fustic, 5 lbs. of logwood, and 20 lbs. of madder. Cool to 180° F., and enter the prepared wool. After well handling, boil slowly for half an hour, adding a solution of 2 lbs. of sulphate of copper. Cudbear, camwood, or peawood, may be used instead of madder. Turmeric is too fugitive to be employed with chrome colours.

A Cheap Olive.

For 100 lbs. of wool. Boil for one hour 30 lbs. of fustic, 6 lbs. of logwood, and then add 10 lbs. of sumach, 5 lbs. of madder, 10 lbs. of red sanders, and

3 lbs. of tartar, boiling for ten minutes. Cool to 180° F., and enter the wool, boiling for one hour. Then add a solution of 2 lbs. of sulphate of copper, again boiling slowly for half an hour. Darken with 5 lbs. of copperas. When the wool has become even, cool the dye and add two pails of urine.

Olive on Zephyr.

For 100 lbs. of yarn. First boil the yarn for one hour in a solution of 20 lbs. of alum, 5 lbs. of tartar, and 2 lbs. of sulphate of copper. Various shades may be obtained upon the prepared wool with fustic, turmeric, orchil, extract of indigo, and picric acid.

BROWNS.

Chrome Brown.

For 100 lbs. of fabric. Boil for one hour in a bath of 2 lbs. of bichromate of potash and 5 lbs. of tartar. Then prepare a fresh kettle with 10 lbs. of peachwood, 1 lb. of logwood, and 1 lb. of tartar, boiling for ten minutes. Cool to 175° F., entering and boiling the fabric for half an hour. The above proportion of tartar and chrome should be strictly adhered to, in order that the colour may become even.

Chrome Red-Brown.

Prepare as for chrome brown. Then produce the desired shade by means of fustic or picric acid. Evenness can be attained by employing sufficient tartar.

Camwood Brown.

For 100 lbs. of wool. Boil until thoroughly incorporated 100 lbs. of camwood, 20 lbs. of sumach, 5 lbs. of logwood, and 2 lbs. of tartar. Cool to 190° F., boiling the wool, after careful handling, for one hour. Add a solution of 2 lbs. of sulphate of copper, again boiling for half an hour. Darken with a solution of 6 lbs. of copperas; and, to obtain a deeper shade, add 3 pails of urine. Remove and cool quickly.

Fast Brown.

For 100 lbs. of wool. Boil for a few minutes 15 lbs. of camwood, 30 lbs. of madder, 10 lbs. of fustic, 15 lbs. of sumach, 5 lbs. of logwood, and 2 lbs. of tartar. Cool, and enter the wool, boiling for one hour, adding afterwards 2 lbs. of sulphate of copper. Darken with 6 lbs. of copperas, and deepen with 3 pails of urine, or with soda.

Another fast brown, but more expensive than the former, may be coloured by the following method. For 100 lbs. of wool:—Dissolve 20 lbs. of alum, 3 lbs. of tartar, and 6 lbs. of muriate of tin, and boil the wool for ten minutes in the solution, allowing it to remain over night. To a kettle of fresh water at 140° F., add 100 lbs. of madder; and handle the wool in this bath for one hour and a half, boiling for twenty minutes. Remove, cool, and rinse, finishing to the required shade in the blue vat.

Light Brown.

For 100 lbs. of wool. Boil 15 lbs. of fustic, 10 lbs. of madder, 12 lbs. of camwood, 2 lbs. of tartar for ten minutes. Cool to 180°, and enter the wool,

handling well. Boil for one hour; and add 11 lbs. of sulphate of copper. Boil again for twenty minutes; and darken with 2 lbs. of copperas.

Browns on wool should never contain an excess of chrome or peachwood.

Bismarck.

For 50 lbs. of fabric. Dissolve 10 lbs. of alum, 2 lbs. of sulphuric acid, 2 ozs. extract of indigo, 1 oz. of fustic, 3 ozs. of madder. Cool and enter the fabric. Boil for half an hour. Remove, cool, and rinse. Pass the fabric next through a cold bath of 3 lbs. of peachwood, 5 lbs. of fustic, and 1 lb. of logwood, with 8 lbs. of dissolved alum. Cudbear, orchil, or magenta and pieric acid may be substituted for the madder, sometimes with the advantage of greater evenness of colour.

Aniline Bismarck.

For 50 lbs. of part cotton fabric. Dissolve 1½ ozs. of aniline brown in boiling alcohol. Enter the goods at 170° F., and handle until even; then colour the cotton as for cotton warps. A bath of strong alum water, sulphuric acid, cudbear, indigo-extract, fustic, or picric acid will yield a good Bismarck with mousselines or thibets.

On zephyr, Bismarck of any desired shade may be obtained according to the following method, by varying the strength of the red, blue, and yellow dye materials:—For 100 lbs. of yarn. Boil the yarn for one hour in a bath of 20 lbs. of alum and 5 lbs. of crude tartar. Add a small quantity of sulphuric acid, cudbear, fustic, or picric acid, and indigo-extract; ½ lb. of cudbear, 5 lbs. of fustic, and 1 oz. of indigo-extract are in good proportion.

Mode with Indigo Bottom.

For 100 lbs. of wool. Colour lightly with indigo-blue. Prepare a beck at 180° F., with 2 lbs. of tartar, 15 lbs. of fustic, 6 lbs. of cudbear, and 8 lbs. of madder. Enter the wool and boil for one hour. Darken with copperas, or deepen with sulphate of copper.

Mode without Indigo.

For 100 lbs. of wool. Prepare a bath with 2 lbs. of tartar, 5 lbs. of sumach, 1 lb. of logwood, 4 lbs. of fustic, 2 lbs. of cudbear, and 5 lbs. of madder. Enter the wool at 180° F., boiling slowly for one hour. Darken with 2 lbs. of copperas, boiling for twenty minutes. Remove and expose to the air; cool for half an hour and rinse. Smaller quantities of dye-stuff in the same proportion to each other will yield lighter colours.

DRABS AND SLATES. Drab.

For 100 lbs. of wool. Dissolve 2 lbs. of tartar, 5 lbs. of camwood, 3 lbs. of sumach, 3 lbs. of fustic, and 1 lb. of logwood. Enter the wool at 180° F., boiling for one hour. Then add 3 lbs. of copperas in solution, and again boil for twenty minutes. Cool, expose to the air, and rinse.

Another drab may be obtained with a bath of 2 lbs. of tartar, 1 lb. of madder, 1 lb. of camwood, 1 lb. of cudbear, 1 lb. of fustic, 1 lb. of logwood, and 1 lb. of sumach. Proceed to darken, air, and rinse as before.

Slate.

For 100 lbs. of wool. Prepare a bath with 2 lbs. of tartar, 2 lbs. of sumach, 3 lbs. of logwood, and 2 lbs. of cudbear. Enter the wool at 180° F., and boil slowly for one hour. Darken with a solution of 3 lbs. of copperas. After twenty minutes remove, air, and rinse.

Purple Slate.

For 100 lbs. of wool. Prepare a bath with 2 lbs. of tartar, 3 lbs. of sumach, 1½ lbs. of logwood, and a hot alcoholic solution of 2 ozs. of aniline purple. Enter the wool at 180° F., and boil slowly for one hour. Darken with 2 lbs. of copperas. Handle, cool, rinse, and dry.

Stone Colour.

For 100 lbs. of wool. Prepare a bath with 2 lbs. of tartar, 4 lbs. of sumach, 1 lb. of logwood, 5 lbs. of fustic, and 2 lbs. of madder. Boil the wool slowly for one hour; darken with 3 lbs. of copperas.

Silver Grey.

For 100 lbs. of wool. Prepare a bath with 1 lb. of crude tartar, \(\frac{1}{4}\) lb. of nut-galls, \(\frac{2}{3}\) lb. of cudbear, and \(\frac{1}{4}\) lb. of logwood. Enter the wool at 180° F., handling well. Then increase the temperature to 200° F. for one hour; cool and darken with copperas. When even, remove, air, and rinse.

Lavender.

For 50 lbs. of fabric (thibets or zephyr). Prepare a bath, at a temperature of 180°, with 5 lbs. of alum, 5 lbs. of cream of tartar, 6 ozs. of indigo-extract, 6 ozs. of cochineal paste. Enter the cloth and boil until even. If the thibets are of mixed silk, the silk will remain uncoloured; it may be dyed red by substituting cudbear or orchil for the cochineal paste; or the wool may be coloured mode and the silk a golden yellow by employing cudbear and turmeric instead of fustic and cochineal. Sulphuric acid instead of tartar, cudbear or orchil instead of cochineal paste, are more economical in the case of coarser goods without silk.

PURPLES.

Aniline Purple.

For 100 lbs. of wool. Dissolve 12 ozs. of Perkin's purple in 1 quart of hot alcohol, straining the solution through a flannel sieve. Add 4 lbs. of acetic acid, 4 lbs. of alum, and 1 lb. of tartar. Enter the wool at 175° F., and after handling, bring the bath to a boil for one hour. Should a blue shade be desired, add 3 lbs. of diluted sulphuric acid; if a red shade, the following method is to be preferred:—12 ozs. of Perkin's purple, dissolved and strained as before (Hofmann's purple does not require alcohol). Add separately 2 ozs. of magenta and 4 lbs. of acetic acid. Enter at 170° F., handling quickly at first.

BLACKS.

Chrome Black.

For roo lbs. of wool or fabric. Dissolve $2\frac{1}{2}$ lbs. of bichromate of potash and 2 lbs. of argol. Boil the fabric or wool in this solution for one hour. Cool and rinse.

Boil in fresh water 25 lbs. of logwood and 10 lbs. of fustic, adding ½ lb. of argol, ½ lb. dilute sulphuric acid. Enter the prepared wool. Boil for three quarters of an hour. Remove, cool, and rinse. For orleans and lastings with coloured warps the sulphuric acid must be omitted. A blue-black may be obtained by omitting the fustic and some of the logwood.

Sumach Black.

For 100 lbs. of cloth. Dissolve 40 lbs. of sumach and 2 lbs. of argol. Enter the fabric, boiling slowly for one hour. Remove the fabric, and add to the beck 6 lbs. of copperas and 2 lbs. of sulphate of copper. Enter at 190° F. for half an hour. Remove and air. Cool the dye to 150° F., and add a solution of 4 lbs. of soda-ash. Run through for fifteen minutes, remove, and rinse. This dye upon broadcloth will take colours from the printing block, and may be discharged during steaming if oxalic acid is mixed with the colours.

Fast Black.

This colour prepared without iron, copper, chrome, or logwood is not suited to common goods, but is adapted for application to mixed goods, such as hosiery. Colour the fabric with lac-scarlet. Then pass it through a warm bath of weak soda-lye (about 5 lbs. of soda). Rinse, and finish in the indigovat until black—6 lbs. of indigo to 100 lbs. of fabric.

Cheap Black.

For 100 lbs. of cloth. Boil in a bag for half an hour 25 lbs. of logwood and 10 lbs. of fustic, and to the bath add 3 lbs. of blue vitriol, 1 lb. of tartar, and ½ lb. of hydrochloric acid. Enter the cloth, boil for one hour, and then pass through a warm solution of 5 lbs. of soda. The dye is very fugitive.

Black for Silk-striped Thibets.

For 5 pieces of fabric, each piece weighing 10 lbs. Dissolve 5 lbs. of copperas, 1 lb. of sulphate of copper, 2 lbs. of tartar, 1½ ozs. of chloride of tin crystals, or 3 ozs. of oxychloride of tin.* Enter the fabric over a reel, and boil for one and a half hours. Remove, cool, and rinse. Prepare a fresh bath with 25 lbs. of logwood. Cool to 180° F., and enter the prepared goods, handling them quickly. Cool to 130°, adding 2 lbs. of liquor ammonia. After fifteen minutes rinse and dry.

COLOURS ON WOOL AND WARPS. Slates and Modes on White Warps.

For 15 pieces of goods, each piece weighing 10 lbs. Dissolve 20 lbs. of alum, 15 lbs. of sulphuric acid, 2 lbs. of extract of indigo, 6 lbs. of cudbear, 1 oz. of aniline purple dissolved in hot alcohol. Cool to 180° F., and enter the fabric, reeling for one hour, and raising the temperature to boiling. Remove and rinse. Then reel through a cold bath of 50 lbs. of sumach for half an hour, and afterwards through a cold bath containing a solution of 10 lbs. of copperas, 2 lbs. of sulphate of copper, and 2 lbs. of nitrate of iron. Remove and rinse.

^{*} Obtained by passing chlorine through a solution of muriate of tin.

Magenta on Cotton Warps.

For 50 lbs. of fabric. First colour with the magenta as for wool. Then take the fabric through a cold bath of 2 lbs. of nut-galls, handling for twenty minutes. Dissolve 1½ ozs. of magenta crystals, adding the solution to a cold bath. Enter the goods fresh from the nut-galls; handle for half an hour. Rinse and dry.

Purple on Cotton Warps.

For 50 lbs. of fabric. Colour first a light purple, and then pass through a bath containing 2 lbs. of nut-galls. Dissolve 2 ozs. of aniline purple in alcohol, and with it prepare a cold bath. Enter the goods. Reel quickly at first, then slowly for half an hour.

Scarlet on Cotton Warps.

For 50 lbs. of fabric. Colour first scarlet as for wool. Then pass through a cold bath containing a large quantity of sumach for half an hour, and afterwards through a solution of 8 lbs. of nitrate of tin. Have the mordant as little diluted as possible, and handle for ten minutes. Then take the fabric through a cold bath of 8 lbs. of alum and 5 pails of fustic liquor, to which add 1 lb. of whiting or chalk. Afterwards pass through a cold bath containing 25 lbs. of peachwood.

Saxon Blue on Cotton Warps.

For 50 lbs. of fabric. Colour first as for wool. Then handle for fifteen minutes in a cold bath containing 3 lbs. of nitrate of iron and 2 lbs. of muriate of tin. In a fresh kettle dissolve 1 lb. of yellow prussiate of potash, to which add 2 lbs. of sulphuric acid. Enter cold, and pass again through the mordant. Rinse and dry.

Aniline Blue on Cotton Warps.

For 50 lbs. of fabric. Colour first as for wool. Then colour the cotton with the prussiate of potash and the nitrate of iron alternately until the desired shade is obtained.

Black and Orange on Cotton Warps.

For 50 lbs. of black wool with white warps. Run 10 lbs. of the cloth at a time through a cold beck of 10 lbs. of acetate of lead, previously boiled for twenty minutes with 5 lbs. of litharge. Thence take each 10 lbs. through a cold weak lime bath, and again through a warm bath containing 10 lbs. of bichromate of potash. Again through weak lime water. In colouring orange on cotton, it should always be borne in mind that the fabric should not be taken directly from the lead beck into the chrome in order to prevent the occurrence of bleared stripes.

Green on White Warps.

For 50 lbs. of fabric. First colour the wool green as for yarn. Then colour the warp with Saxony blue, passing the blued fabric through a beck containing rolbs. of alum and rolbs. of fustic liquor. For an intensely yellow shade citron bark or turmeric may be added.

RANDOMS, OR CLOUDED YARNS.

On the large scale the random yarns are coloured in machines, but the following method can be recommended for colouring in the ordinary manner:—
The yarn is first scoured with soap and bleached, and 15 to 20 lbs. are parted off into handfuls of about 1 lb. of yarn each. The yarn thus mechanically prepared is laid in a bath of water, slightly acidified with muriate of tin to neutralise the small quantity of alkali still remaining in the yarn.

Scarlet Random.

A kettle should be prepared of the following dimensions:—5 feet in length, 2 feet 2 inches in width, and 7 inches in depth, made of copper thickly tinned. The bath may be heated by steam or by fire. The kettle should be filled with water to within 2 inches of the rim, and the water raised to a boil. Then add 1½ lbs. of ground cochineal, 2 ozs. of flavine, ½ lb. of tartar, 3 lbs. of scarlet spirit (muriate of tin), and 2 ozs. of tin crystals. Boil for five minutes, then remove the source of heat. The height of the liquid in the kettle should be adjusted to the depth of dye required upon the yarn; if the level of the dye is low there will be much white and little scarlet; if high, much scarlet and little white.

The yarn must now be hung upon sticks in the following manner:-The kettle being 26 inches wide, the sticks to bear fairly on the rim should be at least 30 inches long, 3 inch broad, and 1 inch thick. Taking two sticks in his right hand and one handful of the soaked yarn in his left, the dyer hangs it upon the sticks skein by skein; he then grasps one of the sticks in the middle of its length, and allows the other to remain supported by the yarn. The upper stick is then placed against two pegs 21 inches from another pair of pegs, each peg of the pair being 26 inches from the other. The yarn being drawn from the upper stick, a second stick is laid on the nearer side of the nearer pair of pegs, the yarn being then carried back to the more distant pair of pegs, and there secured by another stick. The yarn thus folded backward and forward is thoroughly wetted with cold water, and is then immersed in the kettle. All the contents of the sticks may be handled at one time by means of a pole passed under the whole series of sticks. After twenty minutes the yarn will be a good scarlet, and may be taken out and rinsed. The rinsing water should be allowed to flow down upon the yarn, so that the dye may not be carried on to the whites. By this method one man can colour 150 lbs. of yarn daily without assistance.

Orange Random.

The yarn should be soured as for scarlet. The kettle is prepared with ½ lb. of flavine, ½ lb. of tartar, 2 lbs. of muriate of tin, 2 ozs. of tin crystals, 6 ozs. of cochineal, and the bath is raised to the boiling-point for ten minutes before the wet yarn is entered. In twenty minutes remove and rinse.

Saxon Blue Random.

Prepare the kettle with 6 ozs. of extract of indigo, 2 lbs. of alum, 1 lb. of sulphuric acid, and ½ lb. of muriate of tin. Raise the temperature to 190° F., and then remove the source of heat. Enter the wet yarn. The yarn may be bleached after colouring, being well rinsed after removal from the sulphurhouse.

Prussian Blue Random.

The yarn must be unbleached. Soak the yarn in the dilute muriate of tin bath; and prepare the kettle with ½ lb. red prussiate of potash (to every 15 lbs. of yarn), adding ½ lb. of sulphuric acid and 1 lb. of muriate of tin. Heat to 120° F., and enter the yarn, raising the bath to the boiling-point in the course of an hour. Remove, cool, and expose to the oxygen of the atmosphere for several hours; then rinse. Should the yarn show green spots a few minutes' steaming will remedy the defect.

Magenta Random.

Half an ounce of magenta crystals (to 20 lbs. of unbleached yarn) dissolved in a bath heated to 170° F. Treat as for Saxon blue; rinse quickly, and bleach in the sulphur-house. Rinse again in cold water.

Purple Random.

For 20 lbs. of yarn. Soak the yarn in water acidified with sulphuric acid (1 lb. of acid to 6 pails of water). Then enter it in a bath containing ½ oz. of aniline purple dissolved in hot alcohol, to which is added 1 lb. of acetic acid. Heat to 160° F., and enter the yarn in one lot. The yarn should be bleached after colouring.

CHAPTER XIII.

SILK.

SILK is valued on account of its high gloss, its fineness and great strength, and the beautiful colours it assumes in the dye-beck. It is the produce of an insect, or rather the larva of an insect known as Bombyx or Phalæna mori. The insect, and the tree upon the leaves of which it feeds, are natives of China, where, according to the historical accounts, silk-worms have been reared, and silk woven into tissues since the year 2698 B.C. From China the cultivation of the mulberry tree and the rearing of silk-worms became introduced into Persia and Hindostan; while sericiculture has been but more recently known to Europeans. In France the mulberry tree and the worm were first cultivated about 1494.

Silk, like the web of the spider, is a secreted substance, that is, it is ejected in a liquid state from the body of the insect, and solidifies immediately on contact with the air. The spun fibre averages in length 350 metres; its diameter never exceeds 108 or the of a millimetre. Viewed under the microscope it has a somewhat flattened cylindrical appearance. Every fibre consists of two distinct parts, an external envelope and an interior textile fibre or true fibroine. The external layer consists of a mixture of albumenoid, nitrogenous, and fatty-resinous matters, to which is sometimes added a colouring matter.

With the exception of MM. Roard and G. J. Mulder, no scientific man has attempted the investigation of the constitution of silk. M. Roard extracted by means of alcohol from raw silk—(1) a wax-like substance similar to the cerotic acid, C27H54O2, of bees'-wax; (2) when raw yellow silk was experimented upon, a colouring-matter incorporated with a brown-red resinous substance was found. According to M. Mulder, the latter can be separated by repeatedly washing with an aqueous solution of caustic potash. White, as well as yellow, silk, when raw, yields upon treatment with boiling water a nitrogenous matter, which in its character and composition bears a close relation to gelatine, and, according to M. Mulder's researches, is identical therewith. When raw silk has been treated consecutively with water, alcohol, and ether, it yields on treatment with concentrated and boiling acetic acid two different nitrogenised substances, one of which being soluble in the acid behaves with reagents similarly to a solution of albumen in acetic acid, while its percentage composition is that of albumen, although it differs in some respects from the white of eggs. The other nitrogenised substance is insoluble, and consists of pure fibroïne. Silk therefore contains in raw state—(1) cerotic acid; (2) a red colouring-matter, not met with in white silk; (3) fatty substances; (4) resinous matter; (5) a nitrogenised substance soluble in boiling water or gelatine; (6) a nitrogenised substance insoluble in boiling water, but soluble in boiling concentrated acetic acid; (7) and finally, fibroïne.

An analysis of silk, by M. Mulder, gave for 100 parts:--

					Yell	low Naples Silk.	White Silk from the Levant.
Fibroïne						53'37	54°04
Gelatine						20.66	10.08
Albumen						24.43	25.47
Wax						1.39	1.11
Colouring-n	natte	er				0.02	emop
Fatty and re	esino	ous n	natte	ers		0.10	0.30

Fibroïne has the appearance of silk, but is softer, more flexible, and not so strong. Heated on platinum foil it swells up, and, bursting into flame, burns, leaving a voluminous coke, which emits a peculiar odour. It is insoluble in neutral solvents and in acetic acid. Fibroïne, as well as silk, is soluble in an ammoniacal solution of oxide of copper, Schweitzer's reagent; neither are acted upon by a solution of oxide of copper in carbonate of ammonia. A solution of silk or fibroïne in Schweitzer's reagent is not precipitated either by salts, sugar, or gum, as in the case of a solution of cotton in the same reagent. Dilute acids precipitate a flocculent mass from the solution of silk. According to M. Schlossberger, an ammoniacal solution of oxide of nickel behaves with silk similarly to Schweitzer's reagent, but does not act at all upon cotton. The fibroine of sponge is not acted upon by an ammoniacal solution of either nickel or copper. A solution of basic chloride of zinc at 60° Baumé dissolves in the cold, and more rapidly when aided by heat, a considerable quantity of silk, forming a viscous, syrupy solution, which, acidulated and then submitted to dialysis, attains the consistency of a thick starch paste; when a more dilute solution is submitted to dialysis, a liquid is obtained which, on being evaporated to dryness, yields a golden-coloured varnish, and this varnish raised to a temperature approaching incipient red-heat assumes, immediately before its decomposition, a beautiful groseille red tinge. When silk is acted upon in the cold by strong sulphuric acid, it yields a viscous bright brown-coloured solution, which turns red, and becomes coloured a deep brown when heat is applied. Water does not precipitate the solution, but the solution thus diluted is precipitated by tannic acid. Nitric and hydrochloric acids also readily dissolve silk at the ordinary temperature, and alkalies precipitate the solution. When silk is afted upon by nitric acid and heat applied, it is converted into oxalic acid. Although silk is not dissolved by dilute solutions of caustic alkalies, these should not be applied to silk for any purpose, because they cause deterioration of the fibre, removing the gloss and brilliancy. Concentrated solutions of caustic alkalies dissolve silk and fibroine, and the solution is precipitated by water and dilute sulphuric acid, but the precipitate obtained is altered in composition. When fibroine is heated with caustic potash it is converted into oxalic acid. The alkaline carbonates and ammonia do not dissolve silk; and ammonia may be advantageously employed in the cleansing of silk, especially if diluted with both water and pure spirits of wine. Many shades of dyed silk will not, of course, withstand this treatment. Fibroïne does not contain sulphur, and the two nitrogenised substances which accompany fibroïne are also free from sulphur. Fibroïne yields 0.3 per cent of ash composed of sulphates, chlorides, alkaline phosphates, phosphate of lime, and magnesia, oxides of iron, manganese, and alumina.

Bleaching Silk.

Silk as obtained from the cocoon is unfit for use, even when it is desired that it should be woven into those extremely fine tissues known as silk gauze, which is made of raw silk thread. For this purpose it is necessary that the raw silk from the cocoon should be submitted to some mechanical operation by which a number of the fibres may become united or spun together. But our province is not to treat of the processes of spinning; we shall therefore proceed to the means of removing the colouring-matter from the raw silk, as well as the gummy matter and wax. The oldest process in use for this purpose is boiling with soap, and is the only one which can be advantageously as well as safely employed. Raw silk loses during this process 25 to 30 per cent of its weight. At the first boiling the quantity of soap taken is 30 per cent of the weight of the silk; a second boiling is effected with 15 per cent of soap. Great care is required in the management of these operations, as experience has proved that the silks from Piedmont, the Cévennes, and Bengal cannot withstand a prolonged action even of soap without becoming very seriously weakened in strength.

Sometimes silk is treated with a weak alkaline bath composed of 12 per cent of the weight of the silk of caustic soda; but although by this operation silk loses only 12 per cent in weight it becomes very dull and the fibre brittle. Another method of treating silk is to immerse it for a few minutes in a bath composed of I part of nitric acid, 4 parts of hydrochloric acid, and sufficient water to obtain at a temperature of 30° to 35° a liquid of a density of 15° to 18° Baumé. The silk is immersed in this liquid after having been steeped in a tepid soap bath containing 10 per cent of soap. As soon as the silk placed in the acid bath assumes a grey tinge it should be removed, washed thoroughly in a large quantity of cold water, and next submitted to the action of the fumes of burning sulphur. In order to augment the whiteness of the bleached silk it is sometimes thought necessary to employ a blue colouring-matter. Baumé has introduced the following method for bleaching and softening silk:-The raw silk is steeped in cold water for a few days to dissolve the gelatine contained. It is next placed for thirty-six hours in alcohol, to which pure hydrochloric acid has been added (96 kilos. alcohol of o.84 sp. gr., and 400 grms. of pure hydrochloric acid). The silk is afterwards washed in cold water and dried. This method is, however, too expensive for use on the large scale, but the results are excellent. As regards the water to be employed in the bleaching of silk, the purest and the freest from lime is the best; the quality of the water is, in France, considered of so much importance that the silk is sent to localities, especially in the Department de l'Ardéche, where the water, owing to the prevalence of granite rock, is almost entirely free from lime salts. Silk is very readily injured by the insoluble lime soap which is formed when soap is dissolved in water containing soluble salts of lime, its softness, strength of fibre, and colour being impaired.

The loss of 25 per cent in weight of so valuable a substance as silk has had the effect of turning the attention of many to the devising of processes for removing the colouring-matter without taking away the gummy substance and the wax which contribute to so large a portion of the loss, but the attempt is futile on the ground that silk cannot be dyed, or at least not uniformly dyed, unless the whole of the gelatine, wax, resinous, and colouring-matters are

removed. Baumé's process leaves in the silk all the albumen; the gelatine, wax, and resinous matters only are dissolved, reducing considerably the percentage of loss. It is stated that the Japanese and Chinese have practical processes for bleaching silk without the use of soap or great loss in weight, but there is no definite information extant.

Means of Distinguishing Silk and Other Fibres.

It is not at all difficult to distinguish wool from silk when attention is paid to the several solvents. There may be added to the information given under the preceding heading the statement of the fact that pure quadrihydrated nitric acid, while it dissolves silk, only colours wool yellow. Wool, owing to the sulphur it contains, becomes coloured black in a solution of oxide of lead in caustic potash. Nitro-prusside of sodium is a more delicate reagent, the wool or silk having been dissolved in a caustic alkali. Silk and wool are dissolved in caustic alkalies when heat is applied; cotton and linen fibres are not affected by similar treatment. Animal fibres emit on combustion the peculiar odour of burnt feathers, become coloured yellow with nitric acid, and red with nitrate of mercury, and are not acted upon during steaming after having been moistened with dilute mineral acids. Cotton, hemp, and flax fibres burn without emitting the peculiar odour, and are strongly attacked during steaming when previously moistened with even very dilute mineral acids.

The microscope, however, affords the most ready method of distinguishing fibres from each other. The fibre of cotton, Fig. 7, appears as a riband twisted spirally, and its characteristics are unmistakable. Flax fibre, Fig. 8, is neither stiff nor twisted, and is distinguished by the narrowness of its inner tube. The fibre of silk, Fig. 10, is perfectly cylindrical throughout, not hollow inside, and the surface is smooth and glossy, whilst woollen fibres, Fig. 9, are scaled and bark-like in appearance. Fig. 11 represents woollen, cotton, and silk fibres as they appear together under the object-glass of a microscope magnifying 120 to 150 times. The sample of cloth to be submitted to examination should be cut up, placed on a slide in water, and covered with a thin piece of glass. Other fibres may be distinguished readily by means of the microscope; and for this purpose the following observations will be found of use:—

Manilla.—Fibrous bundles oval, nearly opaque, and surrounded by a considerable quantity of dried up cellular tissue, composed of rectangular cells. The bundles are smooth; very few partly detached ultimate fibres are seen, and no spiral tissue.

Sizal.—Fibrous bundles oval and surrounded by cellular tissue. Smooth and very few ultimate fibres projecting from the bundles. More translucent than Manilla, and always to be recognised by the large quantity of spiral fibres mixed up in the bundles.

New Zealand Flax, or Phormium Tenax.—In machine-dressed Phormium the bundles are translucent and irregularly covered with tissue. Spiral fibres can be detected amongst the bundles, but not in the same quantity as seen in Sizal. Many more ultimate fibres project from the bundles, which are flat instead of oval. In those places where the bundles are entirely freed from tissue they are generally divided longitudinally into two or more smaller bundles or fasciculi, and in these places the number of half-

detached ultimate fibres is greatly increased; they are, however, rarely broken, most of them having the end perfect. Spiral fibres are here absent. In Maori-prepared *Phormium* the bundles are almost entirely free from

Fig. 7.



tissue, and quite so from spiral fibres. These are always broken up into many fasciculi, which average, perhaps, some twelve or fifteen ultimate fibres in each fasciculus. Many ultimate fibres are semi-detached, and they are

Fig. 8.



Fig. 9.



much more broken than in machine-prepared fibre. For examination of the ultimate fibre, Captain Hutton recommends boiling for two or three hours in a weak solution of potash, and separation of the fibres by dissection under the

microscope in water. The ultimate fibres of Sizal will be found to separate easily, those of *Phormium* with more difficulty, while it will require great care to prevent breaking those of Manilla; this latter fibre will require a much longer boiling to render separation easy. According to Captain Hutton's table

Fig. 11.





of measurements, the average length of the fibre of *Phormium* will be found to be nearly twice that of the others; while the average diameter is not more than half that of Manilla, which is again much less than that of Sizal. The cell wall of *Phormium* is also much thinner than that of either of the other two.

CHAPTER XIV.

POTASH, SODA, AND LIME SALTS.

POTASH.

POTASH, according to the commercial term, but chemically carbonate of potash, KO,CO2, occurs in the inorganic and in the organic kingdoms. In the inorganic state its compounds are found in feldspar, in deposits with rock salt, the mother-lye of saline springs, and in sea-water. But the organic sources are also very important, and include the ash of plants, and the ash of other organic substances. Potash is obtained by elutriation of the ashes of plants, the evaporation of the lye, and the calcination of the residue; this residue, or commercial carbonate of potash, is more or less rich in pure carbonate of potash. The qualities of good potash are that it should be hard, porous, of a white, geen, blue, gray, or red shade, possessing a caustic taste. and the quality of absorbing atmospheric moisture or of deliquescing, being readily soluble in water. The value of potash depends upon the quantity of potash which as carbonate of potash or as caustic potash it contains. The proportion of carbonate of potash can be estimated by various methods giving more or less accurate results. A useful test is the following:-100 grains of well-dried potash are weighed out and dissolved in a beaker. Into another 300 grains of diluted chemically pure sulphuric acid are introduced in the proportion of 100 grains of concentrated sulphuric acid to 200 grains of pure water. The sulphuric acid sets free the carbonic acid of the carbonate. which can be measured by the corresponding loss of weight. Multiplying the number indicating this loss of weight by 100 and dividing by 32 will give the percentage of pure carbonate of potash contained in the sample. It will be necessary, should not the solution of potash be clear, to first filter it, to wash the residue, and to add the wash-water to the filtrate.

The alkalimetric method is grounded upon the fact that caustic potash and carbonate of potash are converted into sulphate upon the addition of sulphuric acid. 100 parts by weight of anhydrous potash will saturate 104 parts by weight of sulphuric acid of 66° B. It becomes then only necessary to add 104 parts by weight of sulphuric acid (66° B.) to 100 c.c. of water in a burette, so that the fluid reaches to 0°. The potash is weighed out in 100 parts, dissolved in water, and the clear solution coloured blue with litmus-solution. The acid is added in small quantities, in order that the mixture may not become much heated. The solution presently acquires a wine-red colour, and the number of c.c. of acid solution required to effect this change will give the percentage of anhydrous potash. The chief impurities of commercial potash are sand, silica, and metallic salts. The sand can in great part be removed by dissolving the potash, and filtering. The silica occurs chiefly as silicate

of potash. Copper salts can be detected by dissolving the potash in hydrochloric acid, supersaturating with ammonia, when, if copper be present, the solution will become coloured blue.

The potash of the market is generally termed pearl-ash or American ash, or salt of tartar. It is not largely employed in printing or dyeing; chiefly in Turkey-red dyeing for the emulsion of oil, and also as a solvent of annatto and safflower.

Nitrate of Poatsh.

This salt, KO,NO₅, occurs native as saltpetre; but it finds no application in dyeing or bleaching.

Bisulphate of Potash.

This salt, containing two equivalents of sulphuric acid to one of potash, is sometimes employed as a substitute for tartaric acid in lower styles of work, but requires care, and is uncertain in its application.

Chromate of Potash.

There are two chromates of potash known, viz., the chromate, KO, CrO₃, and the bichromate, KO, 2CrO₃.

Bichromate or acid chromate of potash occurs in commerce in beautiful red crystals, very easily soluble in water, and is employed in the preparation of yellow, red, and green colours. When blue indigo is impregnated with bichromate of potash and treated with a solution of tartar, oxalic acid, or diluted sulphuric acid, the chromic acid is set free, and the available oxygen converts the indigo into indigo-white. Isatine can be obtained similarly by treating indigo-blue with permanganate of potash or with ferricyanide of potash and lime.

The impurities most generally occurring in bichromate of potash are sulphate of potash, chloride of potassium, and nitrate of potash. Sulphate of potash may be detected by treating the bichromate with hydrochloric acid, and adding chloride of barium, when, if any sulphate is present, a white precipitate is formed. Chloride of potassium may be detected by the addition of nitric acid, and precipitation with nitrate of silver. Nitrate of potash causes the salt to detonate when thrown upon a red-hot plate.

Chromate of potash, or neutral chromate, crystallises in beautiful yellow crystals, easily soluble in water. It can be prepared by adding carbonate of potash to a solution of the bichromate.

Oxalate of Potash.

Oxalate of potash occurs in three varieties, viz., as neutral oxalate, as acid oxalate or binoxalate, and as quadroxalate. The oxalate of potash of commerce is prepared by neutralising oxalic acid with carbonate of potash; and it occurs in white crystals, which may be rendered anhydrous by heat, and then will dissolve in three parts of water. Its chief application is found in printing.

The impurities are sulphate of potash, tartar, and metallic salts. Sulphate of potash may be detected by dissolving a sample of the salt in warm water, and treating with hydrochloric acid and chloride of barium to obtain a white precipitate. Nitrate of silver will yield a precipitate if chloride of potassium is present, excess of nitric acid having previously been added. Tartar gives

a peculiar odour when the salt is submitted to combustion, and leaves a gray or black residue. Most metallic salts can be detected by treating the sample of oxalate of potash with an excess of ammonia, and adding sulphide of ammonium.

Manganate of Potash.

Manganate of potash is obtained by heating peroxide of manganese with caustic potash, dissolving and crystallising; it occurs in crystals of a fine green colour. The evaporation must be conducted in vacuo. The application is limited to the restoration of indigo colours.

Permanganate of Potash.

Permanganate of potash, or chameleon salt, mineral chameleon, occurs in red-purple crystals. It can be obtained by heating peroxide of manganese with caustic potash, and treating the resulting mass with boiling water. The salt can then be crystallised out by evaporation. It is a most powerful oxidising agent, and has recently been applied to the bleaching of animal and vegetable fibres.

Tartar.

The tartar of commerce is obtained from the only available source, from wine tuns, where it is deposited as red tartar, cream of tartar, or bitartrate of potash. Tartaric acid combines with potash to form two salts, the tartrate and bitartrate of potash; the former is very little known, but the bitartrate is extensively employed under the name of argol, red tartar, or simply tartar. It is employed in dyeing in its crude form, but for finer kinds of work it is necessary that it should be twice re-crystallised. It is not readily soluble in water, and at the usual temperature cannot be concentrated to a higher degree than 2° Tw. For cochineal-pink in calico-printing, and for mordanting woollen goods, it is largely in demand, in the latter case being employed with alum and salts of tin. Besides its application as an acid, tartaric acid possesses the remarkable property of masking metals or preventing their precipitation under the influence of potash; thus potash will not throw down a precipitate from a solution of sulphate of copper to which tartaric acid has been added. Many substitutes have been suggested and sold for tartaric acid, but their success has always been doubtful. The purity of tartaric acid or bitartrate of potash can be determined by calcining a sample in a porcelain crucible. If the acid is pure nothing but a black coke will remain, and this will disappear at a higher temperature. The potash salt should leave either a white or grey residue. An admixture of sulphates may be detected by means of chloride of barium. Copper salts may be detected by ammonia, and salts of the protoxide of iron may be deposited as sulphides by sulphide of ammonium after the addition of ammonia.

Potash Water-Glass.

Potash water-glass, KO,SiO₂, is made of 45 parts of pulverised quartz, 30 parts of potash, and 2 parts of wood charcoal strongly heated together. Potash water-glass occurs in commerce in both fluid and solid form. Fluid water-glass is a yellow, thick, fluid, which by exposure to the air suffers little conversion. It colours litmus paper blue. As a fixing agent water-glass is largely employed in printing.

Chlorate of Potash.

Chlorate of potash, KO,ClO₅, is prepared by passing chlorine into a hot concentrated potash lye, and is separated by cooling the fluid, in which it is not very readily soluble. By heating chlorate of potash the oxygen is set free, and chloride of potassium remains. In dyeing it is used as an ageing material, especially in conjunction with steam, and in several methods to be described in the course of the work. Its chief impurities are chloride of potassium and nitrate of potash.

Hypochlorite of Potash.

Of this salt we shall speak more fully under the head of Chlorimetry. Its formula is KO,ClO; it is a yellow-tinted fluid with a peculiar odour. The chief application is as a bleaching agent. It may be prepared by passing chlorine into a dilute and cold solution of potash until the alkaline reaction ceases.

SODA SALTS.

Carbonate of Soda.

Carbonate of soda, or, simply, soda, NaO,CO2, occurs in commerce as an artificial product, and partly as the result of the calcination of plants. It is also found native in the waters of certain lakes and in sea water. The plants from which soda-ash is prepared grow, and in many instances are specially cultivated, near the sea shore. The genera chiefly employed, in addition to the species of Fucus thrown up by the sea itself, are those known as Salsola, Atriplex, Salicornia, &c. The process of burning is of a most primitive kind. and is conducted in pits dug in the sand of the sea shore. The heat of combustion is generally very intense, and the ash appears as a hard, semi-fused mass, termed in the trade crude soda or soda-ash, or sal-soda. The best variety. termed Barilla soda, is that obtained from Alicante, Malaga, Carthagena, the Canary Islands, and contains on an average 25 to 30 per cent of carbonate of soda. The next place as regards value is held by Blanquette soda imported from Aigues-Mortes, while an inferior variety in common use is the Varec soda, calcined on the coasts of Normandy and Brittany from the Fucus vesiculosus.

The artificial preparation of soda-ash may be considered as one of the most perfect processes of manufacturing chemistry; indeed, one might say the most perfect and complete process that could be devised. The importance of the invention of M. Leblanc is almost without parallel, especially when there is added the improvement of the recovery of the sulphur from the soda-waste. The process consists of four stages, all of which we shall, as briefly as possible, describe under the following heads:—

- r. Sulphate of soda is prepared from salt by treatment with sulphuric acid, or by roasting common salt with a native metallic sulphuret, such as iron pyrites.
- The sulphate is converted into crude soda by roasting with a mixture of chalk and small coal.
- 3. The crude soda is refined by lixiviation and evaporation.
- 4. The obtaining of sulphur from the soda-waste.
- 1. Sulphate of soda is generally obtained by treating common salt with sulphuric acid, the hydrochloric acid gas being condensed in condensing- or

so-called coke-towers. These towers are stone built, the stone being of a kind not acted upon by hydrochloric acid, cemented with coal-tar and fire-clay. The dimensions of the towers vary between 36 and 42 feet for the height, and 4 to 5½ feet internal width. A wall divides the tower nearly throughout its length into two compartments, the dividing wall being carried to within a short distance of the top of the building. The two compartments are filled with pieces of coke resting on a perforated stone floor, and over the surface of the coke, from the top of the tower, water is caused constantly to trickle. The gas from the decomposed salt is conducted by stoneware tubes to these towers, and is there condensed, so that only a fraction of a per cent escapes into the chimney stalk, with which the second compartment of the coketower is connected.

The furnace in which the salt is decomposed consists of two muffles. One of the muffles is of fire-brick, and encloses a space of 30 feet in length by 9 feet in width, vaulted and so provided with flues that the flames may have complete circulation. The other muffle is of cast-iron, the interior forming a segment of a circle of 9 feet diameter, and 1 foot 9 inches in depth. A lid, also of iron, is provided with two openings, one of which communicates with the second muffle, while the other serves for the introduction of the salt. Half a ton of common salt having been introduced into this muffle, sufficient sulphuric acid (1.7 sp. gr.) is added to form a neutral sulphate. 95 parts of acid of 1.7 sp. gr., or 104 parts of an acid at 1.62 sp. gr., are required to completely decompose 100 parts of salt. When the mixture of acid and salt is dry it is raked over into the second muffle, kept at a bright red-heat to expel the hydrochloric acid gas. Many large firms in this manner decompose 500 tons of common salt per week.

2. The next part of the process consists in the conversion of the sulphate into crude soda; and this is effected by submitting a mixture of—

 Sulphate
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...

to fusion in a reverberatory furnace. Another mixture of-

 Sulphate
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...

is preferred in some works. The furnace employed is generally a balling furnace, shown in Fig. 12. Mr. Wright has found that the loss of soda amounts during this process to 20 per cent of the sodium contained in the sulphate, as in the following proportions—

20.24

The composition of the crude or ball soda may be represented by the following percentical analysis:—

Carbonate of soda			
Sulphuret of calcium			
Caustic lime	 	 	 IO
Carbonate of lime	 	 	 5
Foreign matter	 	 	 IO

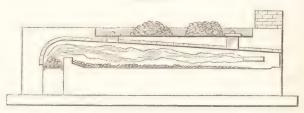
3. The next stage is the refining of the crude soda by lixiviation and evaporation. 100 parts of raw soda have been found to yield—

Soluble matter.			1 +	 	45.0	parts
Soda-waste .	٠	• •		 	55.7	22
					100.7	5.9

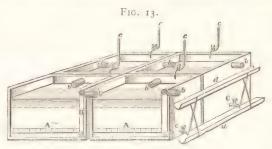
We shall presently see how this waste is made a source of profit to the manufacturer, but we must now continue to trace the course of the product in which our reader is immediately interested.

The lixiviation can be effected by simple filtration, the lumps of crude soda being generally placed in tanks with perforated bottoms, but this method entails

Fig. 12.



great labour. The method of lixiviation invented by Mr. James Shanks, of St. Helen's, is the most economical, as well as the most philosophical. The apparatus is based upon the principle that a short column of a liquid of superior density can be made to balance a higher column of a liquid of an inferior density. A series of tanks are placed together, as shown in the woodcut, Fig. 13, each tank being about 7 feet 6 inches broad, by 6 feet in depth.



At the bottom of the tank is a perforated false sheet-iron bottom, A. From the bottom of each tank to the top is carried a pipe, B, to which, at right angles, is fitted a smaller pipe, b, communicating with the next tank. Water can be supplied to each tank from the pipes, c; and by means of the taps, c, the lye can be run off into a trough, d. In the first tank is placed crude soda that

has been thrice lixiviated, and to it is added a very weak soda solution of such a density that it will percolate into the second tank, where it passes over soda that has been twice lixiviated. Percolating to the third tank, it meets with soda having been lixiviated but once; and thence passes into the fourth tank, where fresh soda has been placed. From the last tank it passes to a reservoir. The first tank is now emptied of soda-waste, and charged with fresh ball soda, and the operation reversed. By this method great waste of labour is prevented, as the increasing gravity of the liquor causes it to do its own work, while the high degree of concentration of the lye effects a considerable saving in fuel during evaporation.

The composition of the crude lye may be represented by the following analysis:—

Caustic soda	0 0	 24.200
Carbonate of soda	0.0	 71'250
Chloride of sodium		 1.850
Sulphate of soda		 0'102
Hyposulphite of soda		 0,360
Sulphuret of sodium		 0.235
Cyanide of sodium		 0.087
Argillaceous earthy matter		 1.210
Silica		 0.186
Iron		 traces

100.089

The lye may be at once evaporated to dryness to obtain a homogeneous product containing all the above constituents; or it may be evaporated to a certain degree of concentration, the crystalline carbonate of soda being separated on cooling by means of perforated ladles. The quality of the commercial article is determined by the care with which the evaporation has been conducted. There are several processes in vogue by which the evaporation is well and quickly effected, but upon which it would be out of place to enter here. Tissandier has shown the composition of refined soda to be for five samples the following:—

	I.	2.	3.	4.	5.
Moisture	2.22	3.11	1.12	1.00	0.40
Insoluble matter	0.13	0.23	0.08	_	0.06
Chloride of sodium	12.48	6.41	3.28	2.11	0.68
Sulphate of soda	8.21	3*25	2.12	1.20	0.32
Carbonate of soda	76.67	87.01	92.34	95'39	98.30
	100,00	100,00	100.00	100.00	100,00

While the composition of the soda containing caustic soda was, for four analyses—

		I.	2.	3.	4.
Moisture	 	2.10	1.20	2.48	1.38
Insoluble matter	 	0'12	O.II	0.31	0.00
Chloride of sodium	 	4.32	2.43	3.20	4.11
Sulphate of soda	 	8.80	1.62	2.12	2.20
Carbonate of soda	 	82.47	88.09	84.24	81.67
Caustic soda	 	2.11	6.22	7.13	10.52
		100.00	100,00	100:00	100,00

So far we have dealt with Leblanc's process in its originality; the plan of M. Schaffner for regenerating the sulphur from the soda-waste we will touch upon presently. Meanwhile it will be interesting and instructive to consider the theory of the process as far as we have presented it to our reader. For the elucidation of the theory we are indebted to the researches of Mr. Gossage and M. Scheurer-Kestner. Chemists long held that the calcination of a mixture of sulphate of soda, carbonate of lime, and carbon resulted in the carbon yielding carbonic oxide, and converting the sulphate of soda into sulphuret of sodium, this in turn becoming decomposed by the carbonate of lime, yielding ultimately carbonate of soda, oxysulphuret of calcium, and carbonic acid according to the following formulæ:—

(1). $Na_2SO_4 + 4C = Na_2S + 4CO$.

(2). $2Na_2S + 3CaCO_3 = 2Na_2CO_3 + CaO_2CaS + CO_2$.

But Unger has proved beyond doubt that only carbonic acid, and not the lower oxide of carbon, is formed, the carbonic oxide resulting merely from excess of carbon and its action upon the carbonate of lime. The reduction of the carbonate of lime by the carbon is effected at a much higher temperature than that at which the sulphate is reduced, so that carbonate of soda is formed before carbonic oxide. Unger therefore distinguished three stages in the process, viz.:—

1. During the reduction of the sulphate, the evolution of carbonic acid, according to the formula—

 $Na_2SO_4 + 2C = Na_2S + 2CO_2$.

2. The sulphuret of sodium and carbonate of lime are decomposed—Na₂S+CaCO₃=Na₂CO₃+CaS.

3. The excess of carbonate of lime is reduced by the carbon— $2CaCO_3+2C=2CaO+4CO$.

Theory gives 100 parts of sulphate as requiring only 20 parts of carbon, but

in practice as much as 35 to 75 per cent of carbon is employed.

We now turn to the utilisation of the soda-waste by the process carried out by M. Schaffner. Of the importance of the improvement upon Leblanc's process, it may be stated that the accumulated waste from the alkali works at Dieuze contains, according to M. Oppenheim, £150,000 worth of sulphur.

M. Schaffner's method includes three processes:—

- I. The preparation of the waste liquor, or liquor containing the sulphur.
- 2. The decomposition of the sulphur.
- 3. The refining or preparing of the sulphur for the market.
- r. The soda-waste is permitted to oxidise in heaps in the open air, the result being the formation of oxysulphurets and polysulphurets, and subsequently hyposulphites. The lumps of waste are then lixiviated, and a concentrated liquor obtained, the waste being allowed to remain in the tanks, while heated gases from a chimney are forced through perforations in the bottom of the tanks; after eight to ten hours the liquor is collected in a reservoir.
- 2. The lixiviation liquor is next decomposed by hydrochloric acid in closed stone or iron vessels, sulphurous acid gas being evolved and sulphur precipitated, $CaS_2O_3 + 2HCl = CaCl_2 + SO_2 + S + H_2O.$
- 3. The sulphur is very simply prepared, being mixed with water to a paste, and subjected to the heat of steam at a pressure of 13 atmospheres. The molten sulphur settling to the bottom of the vessel is run off into moulds.

There are many other methods of preparing soda from the sulphate, but we must refer our readers to works on technology for the detail of the several processes.

The value of a soda depends upon the quantity of anhydrous carbonate of soda it contains, ascertained by the following method of titration:—

a titration glass. Into another 500 grains of concentrated sulphuric acid are introduced, and the acid is added to the alkali grain by grain until it reacts neutral to test-paper. The loss in weight is the loss of carbonic acid, and as 41'43 parts by weight of carbonic acid correspond to 100 parts by weight of anhydrous carbonate it is easy to estimate the quantity of true carbonate contained in a given sample. For example: Suppose the loss of carbonic acid equals 38, then

41.43: 100 = 38: 91.7 per cent of anhydrous carbonate of soda.

If the soda should contain caustic soda, this must be converted into carbonate before titration by boiling for some time with carbonate of ammonia.

The soda should entirely dissolve; but if a residue remain this must be repeatedly lixiviated until the wash-water no longer causes turmeric paper to become tinged. This wash-water should be added to the solution, and the titration proceeded with as if the soda were entirely soluble.

When treating of alkalimetry we shall speak in more detail of the process of estimating the value of alkalies.

Silicate of Soda.

Silicate of soda, or soda water-glass (NaO,SiO₂) may be prepared by fusing together 45 parts of quartz sand, 23 parts of calcined soda, and 3 parts of carbon; or more simply by fusing 100 parts of pulverised quartz, and 60 parts of calcined Glauber-salt with 15 to 20 parts of carbon, pulverising the fused mass, and treating it with boiling water.

In a fluid condition water-glass may be directly prepared by heating finely pulverised quartz with a strong solution of caustic soda in an iron vessel under

a pressure of 8 atmospheres.

In a dry condition soda water-glass can be prepared by fusing together the ingredients in the foregoing proportions. Water-glass in a pure state and free from sulphur may be prepared by fusing, for twelve hours, 120 parts by weight of finely pulverised quartz with 100 parts of best calcined soda and a quantity of carbon (coal). By this method a water-glass can be obtained as clear, hard, and colourless as the best window glass. From this product fluid water-glass may be prepared by boiling with copper scales for ten hours until the liquid acquires a density of 34° B. Water-glass thus obtained is especially suited to the printer. It is employed as a substitute for dung, but principally for fixing ultramarine-blue and pigment colours. The colour is well triturated with a solution of silicate at 90° Tw.; then printed on without thickening, dried in a cool place; the colour being fixed by passing the fabric through a solution of chloride of ammonium or of common salt. But an unsatisfactory harshness is imparted to the cloth, and the colour is apt to come away in the fixing bath. It serves also in place of borax in the bath for dyeing Nicholson and Guernsey blues and Pomona greens.

Chloride of Sodium.

Common salt, or chloride of sodium (NaCl), finds but few direct applications in the branch of industry under consideration.

Hypochlorite of Soda.

Hypochlorite of soda, NaO,ClO, also known as chloride of soda, serves as a bleaching agent and in the preparation of several colours. It is prepared by the decomposition of chloride of lime with carbonate or with sulphate of soda, or by passing chlorine into a solution of carbonate of soda.

The bleach liquor is of a yellow colour, with a strong odour of hypochlorous acid.

Hypochlorite of soda can be subjected to the same tests as to strength as hypochlorite of lime, and we shall revert to the subject when treating of Chlorimetry. A hypochlorite of soda bath at 9° B. is obtained when 6½ lbs. of hypochlorite of lime at 8° B. are added to 1½ lbs. crystallised soda. It can be employed in the bleaching of white grounds upon brilliantly coloured cotton fabrics.

Phosphate of Soda.

Phosphate of soda, NaO₃PO₅, is but seldom used in calico-printing. It partakes of the character of a weak alkali, and is used as a solvent for lactarine. As an alkaline salt it causes the precipitation of a greater quantity of iron from citrate or sulphate solutions of iron mordant, and hence gives rise to a depth of colour known as a double shade.

Permanganate of Soda.

Permanganate of soda, NaO,Mn₂O₇, which is employed as often as permanganate of potash for technical purposes, is of high value as an oxidising agent for bleaching or for disinfecting. It may be obtained by fusing in an iron vessel 10 parts of caustic soda with 1 part of nitrate of potash, to which is added in small portions on an iron spatula 6 parts of peroxide of manganese. The fused mass is lixiviated with boiling water, and the salt crystallised out by evaporation. A crude permanganate may be obtained by heating to redness with access of air a mixture of 2 parts of nitrate of soda with 1 part of peroxide of manganese.

Tungstate of Soda.

Tungstate of soda is employed in the fixation of logwood pigments. In colouring sheep's wool it is substituted for tin salts.

Tungstate of soda may be prepared by heating 5 parts of tungstic acid with 5 parts of calcined soda in an iron capsule; the tungstate is obtained by dissolving the fused mass in water, and then concentrating the solution by evaporation.

Hyposulphite of Soda.

This salt is used in fixing aniline greens upon the fibre, and is hence known in the trade as "green mordant." In conjunction with salts of copper it has been employed in the production of so-called "argentine" effects, a thin film of sulphide of copper being deposited on the fibre.

LIME SALTS.

Hypochlorite of Lime.

Hypochlorite of lime, CaO,ClO, generally known as chloride of lime, occurs in commerce chiefly in the solid state. Fluid chloride of lime is simply a milk of lime saturated with chlorine, and appears as a yellow fluid possessing a peculiar odour. As access of air causes decomposition of the fluid chloride, it must be kept in closed vessels. In the solid state chloride of lime is a white mass, very hygroscopic, and easily decomposed by the action of the carbonic acid of the atmosphere. Hypochlorite of lime is most extensively employed as a bleaching agent, in very dilute solutions for the scouring of woven fabrics, in fixing and shading colours, and in printing to remove colours in order to show a white ground. Of the methods of preparing and estimating chloride of lime we shall speak more fully under the head of Chlorimetry.

A solution of hypochlorite of lime has but little effect upon colouringmatters. This influence is increased by the addition of such acids or salts as cause the decomposition of the hypochlorite and the formation of free chlorine or hydrochloric acid. The powerful affinity of chlorine for hydrogen is in most cases the cause of the bleaching power of the hypochlorite of lime, and this affinity may produce its effect in two ways:—

I. By the direct removal of the hydrogen from the organic matter.

2. By decomposing the water in which the hydrogen and chlorine are in combination, and setting free the oxygen to act upon the carbon of the colouring-matter, oxidising it to carbonic acid, and to again combine with the hydrogen to form water.

We know, however, but little of the true action of chloride of lime.

AMMONIACAL SALTS.

Ammonia.

Ammonia is not largely employed in dyeing and printing. It is used in scouring, to fix metallic mordants, to produce with cochineal a crimson colour, to fix murexide, to modify the shades produced by a variety of colouringmatters, but chiefly, as is the case with its salts, for ageing purposes, especially with heavy mordants. When pure it does not leave any residue upon evaporation, and should yield no precipitate with sulphuretted hydrogen. The following table shows the percentage of ammonia according to the density at 62° F.

Sp. gr. of the Liquid Ammonia.	Per cent of Ammonia by Weight.	Sp. gr. of the Liquid Ammonia.	Per cent of Ammonia by Weight.
0.875	34.694	0,030	18.580
0.880	33.114	0.932	16.883
o·885	31.228	0.040	15.202
0.800	26.984	0.942	14.132
0.302	25°493	0.920	12.782
0.010	24.013	0.922	11.444
0.012	22.261	0.960	10.113
0.050	21.118	0.962	8.808
0.922	19.961	0.970	7.211

Carbonate of Ammonia.

Carbonate of ammonia (NH₄O,CO₂), occurs in commerce as a white crystalline mass smelling strongly of ammonia and soluble in water. It has but a small number of applications in dyeing, being chiefly employed to brighten colours, especially magenta, to form a soap with the grease of certain fibres, &c.

Sal-Ammoniac.

Sal-ammoniac, or chloride of ammonium, NH₄Cl, forms a colourless crystalline mass, the whole of which, when pure, is volatile by heat. The crystals not unfrequently contain salts of iron, contracted from the vessels in which the sal-ammoniac has been prepared. An aqueous solution of sal-ammoniac, in which nitrate of potash has been boiled, should not, after cooling, exhibit a red colouration on the addition of sulphocyanide of potassium. Sal-ammoniac is employed in the preparation of certain baths, as well as in the precipitation of alumina from aluminate of soda. It modifies the action of metallic salts upon organic colours, and is extensively used along with compounds of copper. It serves in the preparation of pink-salt.

Nitrate of Ammonia.

Nitrate of ammonia possesses the property, by means of the ammonia it contains, of depositing from the acetate of alumina baths the mordant in a basic condition, and by the nitric acid it contains to oxidise the protoxide of iron of the iron-bath to a higher oxide. Better results can be obtained in printing catechu shades and garancine colours, with a bath of nitrate of ammonia (1° to 3° B.) than with chlorate of potash.

CHAPTER XV.

ALKALIMETRY.

THE chemical principles employed in the processes of alkalimetry, based upon the law of chemical combination, are to be found described in any elementary work upon the science of chemistry; we shall here detail the technical processes of determining the value of alkalies.

The Test Solutions.

Having decided upon the form of alkalimeter or burette to be employed, it is necessary to prepare the test solutions, or solutions containing a known proportion of the reagent to be employed. The test solutions used in alkalimetry are an acid of known density and a solution of litmus; the latter being coloured blue by alkalies and red by acids serves to indicate that neutral point at which no free acid exists.

The Litmus Solution.

The litmus solution is prepared by pulverising I part of commercial litmus, and digesting it with 8 parts of cold water for twelve hours. The solution should be filtered off, and divided into two portions, to one of which sulphuric acid is added drop by drop until the litmus shows a red tinge. This solution should then be poured into the other. The litmus solution thus prepared is neutral and very sensitive.

Normal Sulphuric Acid Solution.

One volume of ordinary strong sulphuric acid is diluted with 30 volumes of water, and allowed to cool. 10 c.c. of the normal soda solution, to be presently described, to which some litmus solution has been added, are then employed to calibrate the sulphuric acid, water being added to the latter until I volume of the acid is exactly equivalent to I volume of the alkaline solution. Or very excellent results may be obtained by mixing 40 grms. of chemically pure sulphuric acid with 1000 c.c. of water. I c.c. of the normal acid solution then corresponds to 0.04 grm. of sulphuric acid, from which the strength of a solution of soda may be calculated.

Another method of preparing an acid solution of known strength is as follows:—112'76 grs. of pure neutral and anhydrous carbonate of soda are dissolved in 5 fluid ozs. of hot water; the anhydrous soda being obtained by maintaining pure bicarbonate of soda for some hours at a dull red heat in a platinum crucible. This quantity of neutral carbonate of soda corresponds to 100 grs. of pure potash, that is, 100 grs. of potash and 112'76 grs. of neutral carbonate of soda saturate exactly the same quantity of sulphuric acid. This

aqueous solution of carbonate of soda should exactly saturate the contents of an alkalimeter, divided into 100 parts, filled with 1000 water-grains' weight of a solution of 1 part of concentrated sulphuric acid in 10 parts, by measure or volume, of water, so that the litmus solution becomes coloured very slightly red. But should only 90 volumes of the acid be required to saturate the soda solution, it is evident that to render the acid solution of the required strength, there must be added to every 90 volumes of it 10 volumes of water.

The acid solution adjusted for the assay of soda should be of such a strength that 100 divisions of an alkalimeter capable of containing 1000 grs. of water will exactly neutralise 170.98 (in practice 171) grs. of pure anhydrous

carbonate of soda, or 100 grs. of pure soda.

The alkalimeter described by Faraday is suited to the estimation of potash or soda, or of either or both of their carbonates. He says, "Let the tube represented in the margin, Fig. 14, have 100 grs. of water weighed into it; then let the space it occupies be graduated into 100 equal parts, and every

ten divisions numbered from above downwards. At 22'1 parts, or 77'99 parts from the bottom, make an extra line a little on one side, or even on the opposite side of the graduation, and write at it with a scratching diamond soda; lower down, at 48.62 parts, make another line, and write potash; still lower, at 54'43 parts, a third line carb. soda; and at 65 parts a fourth, marked carb. potash. It will be observed that portions are measured off beneath these marks in the inverse order of the equivalent number of these substances, and consequently directly proportionate to the quantities of any particular acid which will neutralise equal weights of the alkalies and their carbonates. As these points are of great importance, it will be proper to verify them by weighing into the tubes first 350, then 513.8, and lastly 779.9 grs. of water, which will correspond with the marks if they are correct, or the graduation may be laid down from the surface of the four portions of fluid when weighed in, without reference to where they fall upon the general scale. The tube is now completed, except that it should be observed whether the aperture can be perfectly and securely covered by the thumb of the left hand, and if not, or if there be reason to think it not ultimately secure, then it should be heated and contracted until sufficiently small." The acid for use with this alkalimeter should have a sp. gr. of 1.1268; it may

POTABH - 50
CARB.SODA - 55
CARB.SODA

be prepared by mixing r part by weight of sulphuric acid of 1.82 sp. gr. with 4 parts of water. This acid having been poured into the alkalimeter to the point marked carbonate of soda should neutralise exactly 100 grs. of pure anhydrous carbonate of soda dissolved in water.

The most perfect method, however, results from the preparation of a normal acid, so adjusted that 100 alkalimetrical divisions will exactly neutralise 1 equivalent of every base. This acid should have a sp. gr. of 1.032, and may be prepared in the manner described by Dr. Ure as follows:—

"Take 53 grs. (I equivalent) of pure anhydrous neutral carbonate of soda, and dissolve them in about I fluid ounce of water. Prepare, in the meantime, the test sulphuric acid by mixing I part by measure of concentrated

sulphuric acid with about 11 or 12 parts of water, and stir the whole well. The mixture having become quite cold, fill the alkalimeter with the cold diluted acid up to the point marked o°, taking the under line of the liquid as the true level, and, whilst stirring briskly the aqueous solution of the 53 grs. of carbonate of soda, pour the acid carefully from the alkalimeter into the vortex produced by stirring, until, by testing the liquor alternately with reddened and with blue litmus paper, or, more conveniently still, with grey litmus paper, the neutralising point is exactly hit." This acid may be termed simply normal sulphuric acid, and every 100 alkalimetrical degrees, or 1000 watergrains' measure of it, contain 1 equivalent or 40 grs. of anhydrous sulphuric acid, capable of saturating or neutralising 1 equivalent or 47 grs. of potash, 31 of soda, 28 of lime, 17 of ammonia, and indeed an equivalent of any other alkaline base.

For further detail as to the preparation of reagents in a state of chemical purity for more delicate estimations than are required in commercial laboratories, the reader should refer to works of scientific research.

Normal Oxalic Acid Solution.

Mohr was the first to substitute oxalic acid for sulphuric acid in the determination of the value of carbonated and caustic alkalies. It is similar in its action upon litmus; and it can be readily and accurately weighed in a dry state. Mohr recommends that the solution be prepared by dissolving 63 grms. of oxalic acid perfectly dry but not effloresced in a litre of water, while a solution of caustic potash is so adjusted that, bulk for bulk, it neutralises the acid, 6 gri grms. of potash or 5.32 grms. of soda should be weighed out, these quantities corresponding to 0.05 of a molecule; so that as 1000 c.c. of the test acid contain a half molecule of oxalic acid, 100 c.c. will exactly neutralise the quantity of alkali. The oxalic acid solution is added to the alkaline solution to be tested with an excess of 5 to 6 c.c.; by this excess the litmus is turned a wine-red. By means of a pipette divided into tenths of a cubic centimetre the alkaline solution is added until the litmus is again coloured blue. The number of c.c. of test acid employed, minus the number of c.c. of alkali employed, gives the percentage of pure carbonate of potash. Thus, if the sample weighed out were 6.90 grms. of the potash, and 72 c.c. of the acid and 6 c.c. of the alkaline liquor were employed, 72 - 6 = 66 per cent of carbonate of potash.

Normal Hydrochloric Acid Solution.

A normal solution of hydrochloric acid contains 36.5 grms. of chemically pure hydrochloric acid in 1000 c.c. of distilled water. I c.c. of the normal acid then contains 0.036 grm. of hydrochloric acid.

Normal Nitric Acid Solution.

A normal solution of nitric acid contains 54 grms. of chemically pure nitric acid in 1000 c.c. of distilled water. I c.c. of the normal acid, then, contains 0.054 grm. of nitric acid.

The Estimation of Carbonated Alkalies.

It is evident from the consideration of the constitution of the carbonated alkalies that the quantitative determination may be effected with sufficient accuracy for commercial purposes in two ways:—

- By estimating the percentage of alkali from the quantity of acid required for neutralisation.
- 2. By determining the quantity of carbonic acid evolved by the addition of an acid.

Besides the methods already detailed in several processes throughout the work, we shall here present to the reader some further modes of estimating the value of a sample of potash or soda-ash.

The operator should commence by taking the alkalimeter in the left hand, filled with the test acid he wishes to employ; the beaker containing the acid solution should be placed upon a sheet of white paper, and a stirring rod provided, with which the solution may be quickly stirred.

If the sample to be tested consists of carbonate of potash the first addition of the acid produces no effervescence, because the carbonic acid expelled instead of being set free from the solution combines with the carbonate of potash remaining undecomposed to form bicarbonate of potash. Care must be taken to drive off the liberated carbonic acid by heat, because the carbonic acid set free exerts an influence in colouring the litmus red, and the acid should be added until the solution assumes a distinctly pink colour. As long as any of the bicarbonate remains undecomposed a vinous colour obtains, and the addition of the acid should be continued until this disappears. The number of divisions of the acid contained in the alkalimeter gives the percentage of real potash. Thus, if 48 divisions have been used, the sample contains 48 per cent of pure potash.

Should Dr. Ure's alkalimetrical method of employing the acid of such a density that 100 divisions correspond to 1 equivalent of base, that is to 47 of potash, a simple proportion sum will give the percentage of potash. Thus, if 105 divisions have been used (that is, the alkalimeter has been re-filled, and 5 divisions of the second charge used), the proportion will be stated as—

$$\frac{47 \times 105}{100}$$
 = 49.35 per cent of pure potash.

Some guide will be given to the operator by the following percentical analyses of potash by M. Pesier:—

	Tuscan Potash.	Russian Potash.	American Potash.	Pearlash.	Potash from the Vosges.	Valen- ciennes Potash Purified.
Sulphate of potash	13'47	14.11	15'32	14.38	38.84	1.20
Chloride of potassium	0.92	2.09	8.12	3.64	9.16	1.60
Carbonate of potash	74'10	69.61	68.07	71.38	38.63	89.95
Carbonate of soda	3.01	3.09	5.85	2.31	4.12	5.13
Insoluble residue	0.65	1.31	3.32	0.44	2.66	_
Moisture	7.28	8.82		4.26	5.34	0.20
Phosphoric acid, lime, silica, &c	0.24	1.04		3.59	1.30	1.33
Alkalimetrical degree	56	23.1	55	54*4	31.6	68.5

The amount of potash yielded by the ash of different plants Dr. Böttger found to be as follows for 1000 parts:—

		-			P	er Mille.
Pine			 	 	 	0.45
Poplar			 	 	 	0.72
Beech			 	 	 	1.45
Oak			 	 	 	1.23
Boxwood			 	 	 	2.52
Willow			 	 	 	2.85
Elm			 	 	 	3.00
Wheat-stray	V		 	 	 	3.00
Rushes .			 	 	 	5.08
Vine-wood			 	 	 	5.20
Barley-stray	N		 	 	 	5.80
Bean-straw			 	 	 	20.00
Vetch-straw	7		 	 	 	27.50
Wormwood			 	 	 	73.00
Fumitory .			 	 	 	79'00

The ash of the beech contained of-

				I CI CCIICI
Soluble salts	 	 	 	21.27
Insoluble salts	 	 	 4 9	78.73

The percentage of soluble salts consisted of-

			Per cent.
Carbonate of potash	 	 	 15.40
Sulphate of potash	 	 	 2.27
Carbonate of soda	 0.0	 	 3.40
Chloride of sodium	 	 	 0.30
			21.27

According to Dr. Hoss, 100 parts of the following woods give-

		Ash.	Potash.
Pine	 	 0.34	0.042
Beech	 	 0.28	0.122
Ash	 	 1.55	0.074
Oak	 	 1.35	0.120
Elm	 	 2.25	0.300
Willow	 	 2.80	0.582
Vine	 	 3.40	0.220
Wormwood	 	 9.74	7:300
Fumitory	 	 21.00	7.990

Calculated from analyses per mille.

Of the method of preparing the potash we need not here speak, except to say that the ash is first lixiviated, the liquor boiled down to obtain the crude potash by evaporation; the crude potash is then calcined. After calcination it is ready for the market, and is of various shades of colour, being either white, pearl-grey, or tinged with yellow, red, or blue. The blue colour is due to the manganates of potash; the red to oxide of iron.

The average composition of the refined potash obtained from the ash of molasses is as follows:—

Carbonate of potasl	h	 	 94.39	88.73
Carbonate of soda .		 	 traces	6.44
Sulphate of potash		 	 0.58	2.27
Chloride of potassiu	ım	 	 2.40	1.00
Iodide of potassium	1	 	 0.11	0.03
Water		 	 1.76	1.30
Insoluble substance	S	 	 	0.15

The crude potash from beet-root sugar works gives on analysis results within the following limits:—

Carbonate of potash	 	 	 32.9 to	79.0
Carbonate of soda	 	 	 14'3 ,,	23'I
Sulphate of potash	 	 	 1.19 "	14'0
Chloride of potassium	 	 	 2.8 ,,	19.6

The percentage of carbonate of potash contained in a solution may, according to Dr. Gerlach, be roughly estimated from the sp. gr. At 15° C. the densities and percentages are:—

Specific Gravity.	Percentage.	Specific Gravity.	Percentage.
1,000	I	1.301	30
1.018	2 \	1.328	35
1.036	4	1.418	40
I*045	5	1'480	45
1.035	IO	1.244	50
1.141	15	1.557	51
1.135	20	1.240	52
1.242	25		

The alkalimetrical estimation of soda-ash is proceeded with in the same manner as that of potash, the test acid being adjusted so as to saturate an equivalent of soda. 10 grms, of the soda-ash are to be dissolved in water, and the solution diluted to 250 c.c. The solution, if not clear, should be filtered. The water itself must be freed from carbonic acid by boiling, or distilled water should be employed. From the filtrate 50 c.c are to be measured out, containing, as 10 grms. were taken, 2 grms. of soda. These 50 c.c. are to be coloured blue with the litmus solution, then titrated with the normal acid solution, of which an excess may be employed, the solution being titrated back with the normal soda solution. Suppose 30 c.c. of normal acid to have been employed together with 4 c.c. of normal soda solution, then as 4 c.c. of acid had been added in excess, the difference shows 26 c.c. to have been necessary for the neutralisation of the alkaline carbonate. As 0.053 grm. of carbonate of soda corresponds to I c.c. of the normal acid solution, we have 0.053 × 26 = 1.378 grm. of carbonate of soda in 2 grms. soda-ash. The percentage can then, of course, be obtained by the following equation:-

$$2:1378 = 100:x$$

or x = 68 g per cent of carbonate of soda. That is, 100 lbs, of soda-ash contain 68 g lbs, of pure carbonate of soda and 31.1 lbs, of impurities,

These impurities generally consist of sulphide of sodium, hyposulphite and sulphite of soda. They can be detected by the addition of ammonia and nitrate of silver, by which a black precipitate is thrown down. If, after heating the solution and adding more ammonia there still remains a black precipitate, the solution contains hydrosulphuric acid and sulphite of soda.

If there be sulphide of sodium present, it will be recognised upon the addition of the normal sulphuric acid by the formation of sulphate of soda and sulphuretted hydrogen, according to the following equation:—

$$NaS + HO,SO_3 = NaO,SO_3 + HS.$$

If sulphite of soda be present, it will be detected by the peculiar odour of the sulphurous acid formed on the addition of the normal test acid, according to the equation—

$$NaO_{1}SO_{2} + HO_{2}SO_{3} = NaO_{1}SO_{3} + HO + SO_{2}$$
.

In the case of hyposulphite of soda the addition of the normal acid causes decomposition into sulphate of soda, water, sulphurous acid, and sulphur.

$$NaO_{1}S_{2}O_{2} + HO_{1}SO_{3} = NaO_{1}SO_{3} + HO_{1}SO_{2} + S.$$

These impurities must be removed before an accurate test can be made, because their action upon the litmus solution would lead to error in the estimation of the amount of acid employed, and consequently the amount of pure carbonate contained in the sample of soda-ash. MM. Fordos and Gelis recommend the changing of the sulphurets, sulphites, and hyposulphites by adding a little neutral chromate of potash to the alkaline solution, to obtain sulphate of chromium, water, and a separation of sulphur. These reactions do not affect the accuracy of the alkalimetrical process.

Estimation of Caustic Alkalies.

Caustic potash, KO, HO, is composed in 100 parts of 83'97 of pure potash, or anhydrous oxide of potassium, and 16'03 of water. It is prepared from a crude carbonate of potash obtained from chloride of potassium, carnallite, vinasse, or other sources, by lixiviating the crude carbonate, and rendering the liquid caustic with quick-lime; or by igniting a mixture of sulphate of potash, limestone, and small coal, and lixiviating with water at 50° to yield at once a solution of caustic potash. It may also be obtained by decomposing sulphate of potash with caustic baryta; by converting chloride of potassium into silico-fluoride of potassium, and decomposing this salt with caustic lime; or by igniting nitrate of potash with copper-scale. The following table shows the relation of sp. gr. to strength in caustic potash solutions:—

Percentage of Potash.	Degrees Beaumé.	Specific Gravity.
4.7	9	1.09
9.2	15	1.11
13.0	19	1.12
16.3	24	1.13
19.5	28	1.53
23*4	32	1.58
32.4	41	1.33
42°9	50	1.25
46.7	53	1.60
51.2	57	1.60

Percentage Potash.	Degrees Twaddle
5.0	10
7.0	14
10.0	19
12.0	24
14.0	29
16.2	34
10.0	40
21.0	45
22.2	50
24.0	53
25.0	56
26 o	60
27.0	63
28.0	66

t c.c. of normal oxalic acid will neutralise 0.047 grm. of caustic potash.

Caustic soda, or hydroxide of sodium, NaHO, occurs in commerce in the mass or in concentrated solutions. Fused hydrate of soda is composed in 100 parts of 77.5 parts of anhydrous soda and 22.5 parts of water. It may be prepared from carbonate solutions by means of caustic lime, or by the ignition of a mixture of sulphate of soda, chalk, and small coal, and lixiviating the crude soda with water at 50°. The lixivium is concentrated to 1.5 sp. gr. to deposit carbonate, sulphate of soda, and sulphide of sodium. The liquor is kept boiling in iron cauldrons, and Chili saltpetre is then added, in the proportion of 3 or 4 kilos. of the nitrate to every 100 kilos. of caustic soda the solution is likely to yield. During the boiling the nitrate of soda causes the evolution of ammonia and nitrogen by acting upon the sulphuret and cyanide of sodium present in the solution. Pauli illustrates the reaction by the following formulæ:—

 $2NaS + 2NaNO_3 + 4H_2O = 2Na_2SO_4 + 2NaHO + 2HN_3$. $5Na_2S + 8NaNO_3 + 4H_2O = 5Na_2SO_4 + 8NaHO + 8N$.

Dalton gives the following table of percentages of caustic soda contained in solutions of the corresponding density:—

. 0	
Percentage NaHO.	Specific Gravity
4.7	1.06
9.0	1.13
13.0	1.18
16.0	1.53
10.0	1'29
23.0	1.33
26.0	1.36
29.0	1.40
31.0	1'44
34.0	1.42
36.8	1.20
41.3	1.26
46.6	1.63
53.8	1.72
63.6	1.85
77.8	2'00

Percentage NaHO.	Degrees Twaddle.
3°5	10
5.0	14
6.2	19
8.0	24
10.0	29
11.2	34
13.0	40
14.2	45
16.0	50
17.5	53
10.0	56
20.2	60
22°0	63
23.0	66

1 c.c. of normal oxalic acid corresponds to 0.031 grm. of caustic soda.

Ammonia, NH₃, is very variously prepared, and a description of the principal processes would be necessarily too long for these pages. The following table shows the percentage of ammonia contained in a solution of the corresponding specific gravity:—

Percentage NH ₃ .	Specific Gravity
5.20	0.978
6.00	0.976
6.20	0.974
7.00	0.972
7.50	0.970
8.00	0.968
8.20	0.962
9.00	0.963
9.50	0.961
10.00	0.959
10.20	0.957
11.00	0.952
11.20	0.953
12'00	0.921
13.46	0'947
17.52	0.932
19.54	0.925
25'39	0.902
26.00	0.000
31.30	0.824
32.20	0.872

I c.c. of normal oxalic acid neutralises exactly 0.017 grm. of caustic ammonia. 5 c.c. of the liquid ammonia to be tested should be taken in a pipette and coloured blue with litmus solution. The normal oxalic acid solution is added from the burette. Suppose 41 c.c. of the normal acid solution to have been required to neutralise the ammonia, the 5 c.c. of liquid ammonia will have contained 0.017×41=0.697 grm. of caustic ammonia. Suppose the liquid

ammonia marks upon the metrical hydrometer the degree 0.94, that is, I c.c. weighs 0.94 grm., the 5 c.c. will weigh 0.94 \times 5 = 4.7 grms. And as the 4.7 grms. contain 0.697 grm. of caustic ammonia, the equation 4.7: 0.697 = Ioo: x gives x = I4.8 per cent of caustic ammonia. That is, that Ioo lbs. of the liquid ammonia contains I4.8 lbs. of caustic ammonia and 85.2 lbs. of water and impurities.

Acidimetry.

Alkalimetry and acidimetry are characterised by precisely the same methods; a normal acid being used to estimate in the one case the percentage of alkali, and a normal alkali in the other to estimate the percentage of pure acid contained in an acid solution.

The litmus solution is, in the same manner as in alkalimetry, employed as an indicator. I c.c. of normal soda solution contains 0.031 of caustic soda, and will neutralise of—

The specific gravity of an acid is determined by the hydrometer, and from the specific gravity the percentage of pure acid can be obtained.

CHAPTER XVI.

CHLORINE, CHLORIDES, AND CHLORIMETRY.

CHLORINE possesses the valuable property of destroying organic pigments, and consequently is of use to the dyer as a bleaching agent. Under the pressure of the atmosphere and at ordinary temperatures chlorine is a gas of sp. gr. = 1'33. Its colour is a yellowish green. Its irritating odour is well known. One volume of water absorbs 2'5 volumes of the gas, the result being known as chlorine-water. The theory of its bleaching properties is based upon its affinity for hydrogen, forming, with the hydrogen of the organic matter, hydrochloric acid. Simultaneously, by the decomposition of the water contained in the organic body, ozone is formed, and the latter oxidises the colouring matter. Thus, in the case of bleaching flax and raw cotton, only the colouring matter and not the cellulose is destroyed.

For purposes of transport it is usual to employ a combination of chlorine with oxygen and a base, as a hypochlorite, and of these combinations we shall speak presently.

The methods of preparing chlorine are very various. They may be divided into two classes—those employing manganese and those which do not. The latter it will be more convenient to describe first. At Mr. Tennant's works, at Glasgow, Dunlop's process is employed, consisting in acting with sulphuric acid upon a mixture of 3 molecules of common salt with 1 molecule of nitrate of soda. Chlorine and hyponitric acid are evolved, the latter being absorbed by passing the mixed gases through concentrated sulphuric acid.

Péligot's method consists in heating 3 parts of bichromate of potash and 4 parts of concentrated hydrochloric acid, to obtain a solution yielding, upon cooling, crystals of bichromate of chloride of potassium, KCl,CrO₃; and this salt heated to 110° yields chlorine.

Messrs. MacDougal, Rawson, and Shanks decompose chromate of lime by hydrochloric acid, with the formation of chloride of chromium, chloride of calcium, and the evolution of free chlorine, according to the formula—

 $2CaCrO_4 + 16HCl = Cr_2Cl_6 + 2CaCl_2 + 3H_2O + 6Cl$.

The chloride of chromium may be precipitated with carbonate of lime, and converted into chromate of lime by ignition.

M. Vogel decomposes chloride of copper by heat, the chloride being mixed with sand, and heated in earthenware retorts to 250°. Chlorine is evolved, and protochloride of copper remains, convertible into perchloride by treatment with hydrochloric acid. 100 kilos. of cupric chloride yield 6 to 7 cubic metres of chlorine.

These are the principal methods without manganese. The action of sulphuric acid upon salt is supplemented by the addition of peroxide of manganese, the result being the formation of sulphate of soda, sulphate of manganese, and chlorine. In some cases, for the common salt is substituted hydrochloric acid, to form sulphate of manganese and water, all the chlorine being evolved.

Undoubtedly the most important plan yet adopted is that of Mr. Walter Weldon. The process is performed in a series of vessels arranged at five successive elevations, so that, after having been pumped up to the highest of them, the liquor operated upon can afterwards descend to all the others by its own gravity. The lowest of these vessels is a well, which is furnished with a mechanical agitator. The slightly acid chloride of manganese liquor with which the process commences runs from the stills in which it is produced into this well, and is there treated with finely-divided carbonate of lime, the action of which is facilitated by energetic agitation. When the neutralisation of the free acid which is at first contained in this liquor, and the decomposition of the sesquichloride of iron and sesquichloride of aluminium which are also at first contained in it, are completed, the liquor is pumped up into settling tanks placed nearly at the top of the apparatus, and known as "the chloride of manganese settlers." It now consists of a quite neutral mixed solution of chloride of manganese and chloride of calcium, containing in suspension considerable quantities of sulphate of lime and small quantities of oxide of iron and alumina. These solid matters deposit in the chloride of manganese settlers, leaving the bulk of the liquor perfectly bright and clear, and of a faint rose-colour. The next step is to run off the clear portion of the contents of the chloride of manganese settlers into a vessel placed immediately below the settlers, and called the "oxidiser." This is usually a cylindrical iron vessel, about 12 feet in diameter and about 22 feet deep. Two pipes go down nearly to the bottom of the oxidiser,—a large one for conveying a blast of air from a blowing-engine, and a smaller one for the injection of steam. The latter is for the purpose of raising the temperature of the contents of the oxidiser when necessary to between 130° and 160° or 170° F. Immediately above the oxidiser is a reservoir containing milk of lime. The oxidiser having received a charge of clear liquor from the chloride of manganese settlers, and this liquor having been heated up to the proper point, blowing is begun, and milk of lime is then run into the oxidiser as rapidly as possible, until the filtrate from a sample ceases to give a manganese reaction with solution of bleachingpowder. A certain further quantity of milk of lime is then added, and the blowing is continued until peroxidation ceases to advance. That point is usually attained when from about 80 to 85 per cent of the manganese present has become oxidised into peroxide. The contents of the oxidiser are now a thin black mud, consisting of solution of chloride of calcium containing in suspension about 2 lbs. of peroxide of manganese per cubic foot; these 2 lbs. of peroxide of manganese being combined with varying quantities of protoxide of manganese and lime. This thin mud is now run off from the oxidiser into one or other of a range of settling-tanks (mud-settlers) placed below it, and is there left at rest until it has settled as far as it will, usually until about one-half of its volume has become clear. The clear part, consisting simply of solution of chloride of calcium, is then decanted, and the remainder, containing

about 4 lbs. of peroxide of manganese per cubic foot, is then ready to be used in the stills. There it reacts upon hydrochloric acid, liberating chlorine, with reproduction of exactly such a residual solution as was commenced with. With that solution the round of operations is begun again; and so on, time

after time, indefinitely.

The quantity of lime which has to be put into the oxidiser, before the filtrate from a sample of its contents ceases to give a manganese reaction, varies very considerably. Recently precipitated protoxide of manganese dissolves very appreciably in neutral solution of chloride of calcium, its solution therein comporting itself with reagents exactly like solutions of manganese salts. It dissolves also in solution of oxychloride of calcium,—that is to say, in solution of chloride of calcium containing dissolved lime; its solution in oxychloride of calcium not giving the ordinary manganese reactions. Hence, even if all portions of the lime added to the chloride of manganese in the oxidiser were capable of acting on chloride of manganese equally readily, manganese could not cease to be so in solution as to be detectable by ordinary reagents until more than an equivalent of lime had been added, --until enough had been added, that is to say, not only to decompose all the chloride of manganese, but also to form a certain quantity of oxychloride of calcium. It is never the case, however, that all portions of the lime used are capable of acting on the chloride of manganese with equal readiness. The lime used always contains a larger or smaller proportion of particles coarser than the rest, which coarser portions cannot of course act so rapidly as the finer portions; and as the decomposition of the chloride of manganese requires to be completed as quickly as possible, those portions of the lime which will not act upon it instantly are scarcely allowed time to act upon it at all. These coarser portions of the lime thus contribute very little to the decomposition of the chloride of manganese, though they afterwards dissolve completely in the hot solution of chloride of calcium, and then play their full part in the reactions which take place during the subsequent blowing. The proportion of lime which does not act on the chloride of manganese varies with the source of the lime, and with the manner in which it is prepared; so that the quantity of lime which has to be added to a charge of chloride of manganese liquor in the oxidiser, before the filtrate from a sample of the resulting mixture ceases to become coloured on addition of solution of bleaching-powder, varies from about 1.15 to 1.45 equivalents. The further quantity of lime which is added after that point has been reached is now usually enough to raise the total quantity to about 1.5 to 1.6 equivalents, being from one-half to six-tenths in excess of the quantity which actually takes part in the decomposition of the chloride of manganese.

"The results," continues Mr. Weldon, "which we have latterly begun to obtain with these proportions of lime are such as our previous experience had not prepared us to expect. Until quite recently, our experience seemed to show that whatever proportions of lime we might use in the oxidiser, we could not obtain products containing less than an equivalent of base or bases per equivalent of peroxide of manganese in them. Now, however, we are regularly obtaining products containing only between 0.9 and 0.7 equivalent of base, and we have occasionally got down nearly to 0.5 equivalent of base. With respect to the conditions which determine the formation of products

containing these low proportions of base, all that I can say at present is that we have begun to make these products, or at any rate to make them regularly, only since we began to considerably increase the quantity of air blown in a given time into an oxidiser of a given size. There can be scarcely any doubt now that products containing at any rate something less than an equivalent of base have been made occasionally, under special circumstances, from the very beginning; but for a long time it was only so very rarely that we seemed to get less than an equivalent of base, and the apparent proportion less than an equivalent was always so small, that we put down the apparent result—a little hastily, as it now appears—to errors of analysis. It is certain, however, that products containing appreciably less than an equivalent of base have begun to be made regularly only since manufacturers who had previously employed one blowing-engine for the process began to use two engines, blowing with both into the same oxidiser, and since other manufacturers began to work with larger blowing-engines than had been used in the process before.

"All that I can learn with respect to the composition of the new products containing less than an equivalent of base tends to show, to my mind, that there are manganites corresponding to nearly all the known carbonates. We already knew of normal manganites, corresponding, say, to normal carbonate of calcium, and of basic manganites, corresponding to Schindler's carbonate of zinc and to Bonsdorf's carbonate of lead. I venture to believe now that there are also acid manganites, corresponding to the bicarbonates, and that

sesquimanganites probably exist as well.

"That hydrated peroxide of manganese, or H2MnO3, is as distinctly an acid as H2CO3 or H2SO3 seems to me to be shown by the fact that if free hydrated peroxide of manganese be boiled with an equivalent of protoxide of manganese, a reaction takes place between the two bodies, the product of which reaction does not absorb oxygen on treatment with air. Of course, if any free MnO remained after boiling the two bodies together, oxygen would be absorbed on subsequent treatment with air. The product is, in fact, precisely the same compound - ordinarily called 'sesquioxide of manganese,' and written Mn2O3-as that which is produced by blowing air into a mixture of protoxide of manganese and water, or in any other way exposing protoxide of manganese, by itself, to the action of the atmosphere at ordinary temperatures; and its formation in the way just stated seems to me to be exactly similar to that, say, of carbonate or of sulphite of calcium by the reaction of H₂CO₃ or of H₂SO₃ upon CaO. Apart from its being thus formed by a reaction exactly resembling the ordinary reaction of an acid upon a basic protoxide, that which is ordinarily called sesquioxide of manganese is really manganite of hydrogen in which H2 has been replaced by Mn, and that it is thus properly manganite of manganese, or MnMnO3, seems to me to follow from the circumstance that, by whatever method this body may have been produced, on treating it with solution of certain salts of other metals ordinary double decompositions occur. Thus, MnMnO₃+CuSO₄ give MnSO₄+CuMnO₃, and MnMnO₃+FeSO₄ give MnSO₄+FeMnO₃. (This latter is a very unstable body, which soon undergoes spontaneous change; but that it is formed and exists for some time I believe to be certain). Moreover, compounds in which the basic Mn of MnMnO3 is replaced by other metals can be formed, not only by the reaction of MnMnO3 itself upon the salts of other metals, but also by the direct reaction of nascent

manganous acid upon protoxides of other metals. For example, as I stated before, whereas if protoxide of manganese by itself be treated with air in the wet way, only one-half of it undergoes peroxidation, the other half being apparently required to furnish base to the half which becomes peroxidised, if a mixture of protoxide of manganese and an equivalent of lime be treated with air in the wet way, the whole of the protoxide undergoes peroxidation, and the lime ceases to be capable of either reacting on chloride of manganese or of dissolving in solution of chloride of calcium. Similarly, if protoxide of manganese, suspended in solution of either baryta, strontia, soda, or potash, be treated with air, baryta, strontia, soda, or potash goes out of solution, and there is formed an insoluble compound containing one equivalent of manganese, three equivalents of oxygen, and one equivalent of barium, strontium, sodium, or potassium, as the case may be.

"With the existence and modes of formation of normal manganites of all these metals we were formerly acquainted; what is new is the apparent formation, under the conditions of working on the large scale at which we have arrived recently, of acid manganites, or double manganites of metal and hydrogen. By far the greater number of batches containing less than an equivalent of base which have been made as yet resemble in constitution one or the other of the two representative batches. In one of the batches of the total manganese operated upon 86.5 per cent had been peroxidised, and for each equivalent of peroxidised manganese present there were 0.85 equivalent of bases. Regarding the constituents of the batch, for convenience, as MnO₂₁ MnO, and CaO, and considering the total manganese present as a thousand equivalents, there were thus in this batch 865 equivalents of MnO2, 135 equivalents of MnO, and o.85 times 865, or 735 equivalents of total bases, 135 of which were MnO, the remaining 600 being CaO. Assuming that the 600 CaO were combined with 600 MnO₂, as normal manganite of calcium, there remained 265 equivalents MnO2 and 135 equivalents of MnO, the proportion of the former to that of the latter being very nearly two to one. These figures I hold to show the existence in this batch of an acid manganite, $MnH_2(MnO_3)_2$, or a compound containing the elements of one of normal manganite of manganese and one of manganite of hydrogen. In the other batch, of the total manganese present 81.5 per cent had been peroxidised, and for each equivalent of peroxide present there were 0.885 equivalent of bases. This batch, therefore, contained 815 equivalents of MnO2, 185 equivalents of MnO, and 536 equivalents of CaO. Assuming, as before, that all the lime existed as CaMnO3, there were left 279 MnO2 and 185 MnO. This is almost exactly three of the former to two of the latter, suggesting the existence in that batch of a sesquimanganite of manganese, containing the elements of two of normal manganite of manganese with those of one of manganite of hydrogen. In these batches it is only acid manganites of manganese that I suppose to have existed; but one or two batches have been made, containing not much more than o's equivalent of base, in which I believe that there must also have been an acid manganite of calcium. It may be, of course, that in all batches containing less than an equivalent of base a portion of the manganous acid exists in the free state; but I have not yet met with any instance of a batch, the blowing of which I have known to have been continued until peroxidation had really ceased, and the proportion of base in

which, while less than an equivalent, was such that the batch could not have consisted entirely of acid manganites, in which the peroxide remaining after deduction of the quantity equivalent to the combined lime contained in the batch was in any other proportion to the basic manganese contained in the batch than either that of two equivalents to one or that of three equivalents to two—a fact almost irresistibly suggestive of the two bodies being combined. The circumstance, moreover, that under no known conditions can peroxide of manganese be formed, by treating protoxide with air in the wet way, without some portion either of manganese itself or of some other metal going simultaneously into combination as base, strongly indicates that only salts of manganous acid can be formed in that way.

"The quantity of air which requires to be blown into the oxidiser per given quantity of peroxide of manganese made varies with a considerable number of conditions, but more especially with the depth of the charge operated upon, and with the quantity of manganese contained in a given volume of it. Within all practicable limits, increase of the depth of the column blown into is equivalent to increase of the quantity of air blown; and the more particles of protoxide are contained in a given volume of the charge, the larger is the total surface which they present for the air to act upon, and the greater is the proportion of the total oxygen injected which becomes absorbed. The proportion of the oxygen absorbed to the quantity blown in being of course greatest at the commencement of the operation and afterwards continually diminishing, a time at length arriving, if the blowing be continued long enough, at which no more oxygen is absorbed at all, the proportion of the total quantity of oxygen absorbed to the total quantity blown in is also considerably influenced by how nearly to that point the operation be continued. As an illustration of what is obtained on the large scale, it may be stated that a certain batch contained 1987 pounds of peroxide, reckoned as MnO2, which was made in four hours, by the injection of about 240,000 cubic feet of air, being at the rate of about 120 cubic feet of air for every pound of MnO2 made.

"The quantity of acid consumed per ton of bleaching-powder made by means of manganite mud varies with the degree of care with which the process is performed and with the general skill of the manufacturer, being in some cases very considerably below the average quantity consumed in making a ton of bleaching-powder by means of native manganese, while in other cases it is scarcely at all below that quantity. I believe that a ton of bleaching-powder is never made in this country, by means of native manganese, from less than the acid from 60 cwts. of salt, and only rarely from less than the acid from between 70 and 80 cwts. of salt. At least one manufacturer, however, whose mud contains, as yet, by no means a minimum of base, and who at present follows a method of treating the mud in the stills which is not quite the most economical of acid, is consuming, per ton of bleaching-powder made by means of manganite mud, only 170 cubic feet of acid at 24° Twaddell-a quantity which I believe to be producible, in practice, from less than 48 cwts. of salt. As what one manufacturer is doing can surely be done by all, when equally familiar with the process, I venture to believe that a very considerable economy of acid will eventually be realised by the process everywhere.

"The loss of manganese which occurs in the process at present varies from about 4 per cent to about 10 per cent. The only unavoidable source of loss

is that constituted by the deposit of sulphate of lime and other matters which form in chloride of manganese settlers. These deposited matters have to be removed in the state of thin mud, largely mixed, that is to say, with solution of chloride of manganese. Unless this mud be well washed after its removal from the chloride of manganese settlers, and the washings be returned to the process, the manganese lost with this mud amounts to fully 5 per cent, or even more; but by suitable washing the manganese thrown away with the mud from chloride of manganese settlers can be reduced to below 2 per cent. The only other sources of loss are—leakage of vessels, and the running away of mud by careless workmen with the chloride of calcium solution from the mudsettlers. The former of these sources of loss ought, practically, never to exist, and the latter is now being eliminated at several works by the chloride of calcium solution, instead of being run away directly from the mud-settler, being run first into catch-pools, in which any mud which may be run off with it from the mud-settlers is allowed to deposit.

"Beyond the sulphate of lime and other bodies which are deposited in the chloride of manganese settlers, the only residual product of the process, and the only other thing which has to be thrown away, is solution of chloride of calcium. As this solution represents all the lime and all the limestone used in the process, and two-thirds of the chlorine contained in the acid employed, and as an industrial process is, of course, imperfect in proportion as anything whatever which is manipulated in it has to be simply thrown away, and especially in proportion as its yield of the commodity, the production of which is its sole object, falls below the total quantity contained in the materials used, I have tried to use, in the oxidiser, magnesia instead of lime, afterwards decomposing, by heat, the resulting chloride of magnesium into magnesia, for use over again, and hydrochloric acid. In that form, the process is capable of vielding, undiluted with other gases, all the chlorine contained in the acid employed, and, apart from mechanical loss, employs no materials which are not used over and over again, excepting coal and air. This form of the process has already stood the test of a certain amount of experience on the large scale; and I venture to believe that, when the time shall have arrived when it will be desirable to obtain, from a given quantity of hydrochloric acid, more chlorine than can be obtained therefrom by means of peroxide of manganese recovered by means of lime, peroxide of manganese recovered by means of magnesia will prove to be the reagent by which chlorine can be most economically manufactured."

The various hypochlorites are easily prepared when the chlorine is provided. The most important is that known as chloride of lime.

Chloride of lime, bleaching-powder (or more accurately, according to Fresenius, a mixture of 1 molecule of Ca(ClO)₂ and 2 molecules of basic chloride of calcium, CaCl₂,₂CaH₂O₂+2H₂O), occurs in commerce as a moist white powder, 1 part of which is soluble in 10 parts of water. As a bleaching agent, the presence of an acid is required to develope its full properties—a matter of advantage in Turkey-red dyeing in the production of white patterns by printing on a thin paste of tartaric acid, the fabric being afterwards immersed momentarily in a solution of bleaching-powder. For the acid, sulphate or chloride of zinc may be substituted, the hypochlorous acid being set free, while sulphate of lime and oxide of zinc are thrown down.

In considering the constitution of bleaching-powder it may be useful to record that, kept under pressure or in too tightly-closed cases, it is liable to spontaneous decomposition and explosion, illustrated by the formula—

 $Ca(ClO)_2 + CaCl_2 = 2CaCl_2 + O_2$.

When chlorine is admitted to slaked lime, chloride or hypochlorite of lime is almost immediately formed, but the formation is much retarded if an excess of the gas be present. The theory of the formation is that some of the oxygen of the lime combines with the chlorine to form hypochlorous acid, which in its turn, combining with the undecomposed lime, forms hypochlorite of lime; and that another equivalent of the chlorine combines with the decomposed lime or calcium to form chloride of calcium. A bleaching-powder so constituted should consist of—

Hypochlorite of fime 49'31 per cent. Chloride of calcium 38'28 ,, Water...... 12'41 ,,

but such a verification of theory never occurs in samples of the commercial product, the closest approximation being similar to the result of the following percentical analysis:—

Hypochlorite of	lime		 	 	26.72
Active chloride o	f calcit	ım	 	 	20.72
Excess ,,	22		 	 	4.79
Hydrate of lime			 	 	30.46
Water			 	 	17.31
					100,00

Bleaching-liquor is similarly formed by passing chlorine gas into a solution of lime. If we substitute for the lime a solution of caustic soda or potash, the chlorides of these bases are obtained; they are sometimes employed as weak bleaching agents.

Solutions of hypochlorite of potash and hypochlorite of soda are known in commerce as Eaux de Javelle and de Labarraque. Wilson's bleaching-liquor is a solution of hypochlorite of alumina, obtained by mixing chloride of lime with sulphate of alumina in solution. Ramsay's bleaching-liquor, a hypochlorite of magnesia obtained by adding sulphate of magnesia to a solution of bleaching-powder, is a very energetic preparation, and leaves the fibre more soft and supple than the hypochlorite of lime. Varrentrap's bleaching-powder is a solution of hypochlorite of zinc.

The testing of samples of bleaching-liquors or powders is necessary in order to ascertain the percentage they will afford of active chlorine and hypochlorous acid. The indigo-test is based upon the decolourising effect of chlorine upon organic colouring matters. This test is, however, the most inaccurate, because the chlorisatine resulting from the decomposition of the indigo, being in colour yellow, combines with the indigo to produce a green colour, which admits of little accuracy in noting the exact period of change. The indigo-test has generally given way to the method invented by Gay-Lussac, which is based upon the property possessed by arsenious acid in a solution of hydrochloric acid of becoming oxidised to arsenic acid when in the presence of chlorine and water. One equivalent of arsenious acid thus reacts with 2 equivalents of chlorine and 2 equivalents of water to produce 1 equivalent of arsenic acid

and 2 equivalents of hydrochloric acid. Supposing, then, the equivalent of arsenious acid to be represented by 99, while that of chlorine is 35.5, 99 grains of arsenious acid will correspond to 71 (2 equivalents) of chlorine. It is clear, then, for practical purposes there may be taken 139.44 grains of arsenious acid as corresponding to 100 grains of chlorine. Therefore, if 139.44 grains of pure arsenious acid be dissolved in 3 ozs. of pure hydrochloric acid, and the solution diluted to 10,000 grains measure, each 1000 grains measure will contain 13.944 grains of arsenious acid, equivalent to 10 grains weight of chlorine. This is the arsenious acid test solution. To this solution is to be added a few drops of sulphate of indigo, in order to afford an indication of the point at which the bleaching effect of the chloride of lime solution predominates. The process of titration is proceeded with as in alkalimetry, and the result obtained by a proportional equation.

With the description of another chlorimetric process we shall bring this division to a close. For this method it is necessary to prepare some iodide of potassium-starch papers, by taking a clear solution of starch and dissolving therein some iodide of potassium; filter-paper may then be dipped into this solution, and then cut into small strips. This paper, when prepared in this manner, becomes coloured blue by contact with chlorine and hypochlorites.

The normal arsenious acid solution is prepared from finely-pulverised arsenious acid dried in a desiccator. From this dried arsenious acid 4'95 grms. are weighed out, and dissolved, in the presence of 10 grms. of carbonate of soda, in distilled water, and diluted to 1000 c.c. A c.c. of this solution contains therefore 0'00495 grm. of arsenious acid.

Iodine is very little soluble in water, and is best employed for this purpose in the form of solution in iodide of potassium. There are to be weighed out 12.7 grms. of crystals of iodine, and these are to be rubbed down with 18 grms. of iodide of potassium, in a porcelain mortar, with the addition of a little water. This solution should be diluted to 1000 c.c., and 10 c.c. of this diluted solution should be capable of oxidising 1 c.c. of normal arsenious acid into arsenic acid.

Estimation of the Chlorine in Chlorine-Water.

Two equivalents of chlorine are capable of oxidising I equivalent of arsenious acid to arsenic acid, so that I c.c. of the normal arsenious acid solution corresponds to 0.00355 grm. of chlorine: 50 c.c. of the sample to be tested are to be titrated with the arsenious test-solution until the iodide test-paper is no longer coloured blue. The test may then be discontinued, or, for greater accuracy, the solution may be titrated back with the normal iodine solution, the number of divisions of the iodine solution employed being divided by 10. An example will make the process clear. We have 50 c.c. of the chlorine water to be tested, and we will suppose 34 c.c. of the normal arsenious acid solution to have been employed in the titration, and 18.8 c.c. of the iodine solution in the re-titration, this representing the excess of normal arsenious solution employed. Dividing this number by 10, and deducting the result 1'88 from 34, we have 32'12 c.c. of normal arsenious acid solution really employed. This number multiplied by 0.00355 gives 0.114026 grm. chlorine. The 50 c.c. of chlorine water contain, therefore, 0.114026 grm. of chlorine, and from the equation-

50:0.114026=100:x

we obtain x = 0.228 per cent of chlorine.

Estimation of Hypochlorites.

The hypochlorites are seldom pure, but contain, from the method of their preparation, constituents which more or less directly bear upon the correctness of the observation. Hypochlorite of lime contains besides, as we have seen, chloride of calcium and hydrate of lime. The hypochlorites of potash and soda contain carbonates and chlorides of the respective bases.

Two equivalents of chlorine correspond to r equivalent of hypochlorous acid, or (2 equivalents of chlorine being equal to 71 parts of chlorine) to 71.5 parts of hypochlorite of lime, 74.5 parts of hypochlorite of soda, or 90.7 parts of hypochlorite of potash.

In order to estimate the value of a hypochlorite of lime, 10 grms, of the sample to be tested should be rubbed down with a small quantity of water, to form a smooth milky fluid: this milk should be poured into a mixing beaker, and the residue remaining in the mortar should be washed with water, and the wash-water added to the contents of the beaker. The milky liquid should then be diluted to 500 c.c. 50 c.c. of this solution should then be brought under the burette containing the normal arsenious acid solution, which must be added until the iodide test-paper is no longer tinged blue. Then the solution should be titrated back with the normal iodine solution, until the blue colour is re-established. The number of c.c. of iodine solution employed divided by 10, subtracted from the number of c.c. of normal arsenious acid employed, will give a difference which, multipled by 0.00355, produces the required weight in grammes. For example, suppose 50 c.c. = 1 grm. of hypochlorite of lime, to require 92 c.c. of the normal arsenious acid solution for the titration, and 18 c.c. of the iodine solution for the second titration; then $g_2 - r_8 = g_0 \cdot 2$ c.c., and 90'2 x 0'00355 = 0'32021 grm. of chlorine, or of hypochlorite of lime containing 32.021 per cent of chlorine.

The applications of the salts not described in this section will be found recorded during the subsequent pages of the work.

DIVISION II.

CHAPTER I.

THE GENERAL PRINCIPLES OF THE FIXATION OF COLOURING MATTER UPON FIBROUS TEXTURES. CLASSIFICATION OF DYE-MATERIALS.

THE substances employed industrially to impart colours to textile fabrics are of very various origin and different characters. Some of them play only a subsidiary part, and are removed as soon as the colouring-matter is definitely fixed-such are, for instance, thickeners, acids used as discharges, resists or solvents, oxidising and reducing agents, substances employed only on account of their hygroscopic properties, and some others which, of great utility, have their action unexplained. Other substances, again, concur either wholly or partly to constitute the colour remaining upon the cloth. Indigotine is integrally fixed, while acetate of alumina and chromate of potash are substances employed as agents for the fixing of madder-red and chrome-yellow, deriving their powers from the alumina and chromic acid they contain. All these substances are, therefore, dyes or tinctorial matters, because for the production of madder-red alumina is as necessary as alizarine itself, which is naturally of a pale yellow-red colour. It is clear, however, that in a restricted sense alumina cannot be called a tinctorial or colour-giving matter, considering that it does not impart to tissues, nor is itself possessed of, any colour. Colours likewise exist that directly impart to cloth their own tinge, such as indigotine, carthamic acid, bixine. There also belong to this class the oxides of iron and chromium, and ultramarine. A rather too familiar instance of the tinctorial power of oxide of iron occurs in the "iron-moulding" of linen. But a large number of dyes require the intervention of a mordant. When a substance is dyed red with madder the alumina is the mordant and the alizarine contained in the madder the colouring matter; whilst in the case of chrome-yellow the chromic acid is the colouring matter and the oxide of lead may be called the mordant. Taking the widest limit of this view, it must be admitted that the colour yielded by catechu is the result of the union of catechine with oxygen, the latter acting really as a mordant. But the term mordant is now limited in its application to substances in the solid state. There must be no confusion between the colouring matters and mordants of commerce, and the produce fixed upon the woven fabric; madder, for instance, is commercially a colouring material, and acetate of alumina commercially a mordant, but the immediately effective colouring matter is alizarine, and the active agent of the mordant alumina. The mode of action of mordants is manifold as well as complex, and again differs for different cases. The mordant sometimes serves to render the colouring matter insoluble, and to fix it to tissues for which the colouring matter has itself but little affinity. Again, the mordant may modify or entirely change the shade of the colouring matter; or the mordant may simply render the dye "fast," as it is termed, instanced by the peculiar action of fatty matter in turkey-red dyeing. In another portion of this chapter we shall speak more in detail of the nature and action of mordants.

Colouring matters may, then, be divided into two classes:-

r. Colouring matters that become fixed and exhibit their peculiar colour without the application of an intermediate agent or mordant.

2. Colouring matters fixed by the agency of a mordant with which they combine.

Aniline-red dyes wool and silk without the aid of a mordant, while it has not the least affinity for cotton, hemp, or flax. Animal fibres combine chemically with fuchsine and analogous colouring matters; indeed, many animal substances themselves act as mordants. We have arrived at the conclusion, therefore, that a woven tissue can be said to be dyed only when the dye resists the action of water and of friction. The colouring matter must consequently mechanically adhere to the fibre or be chemically incorporated with it. The theory of the fixing of colouring matter cannot be reduced to a single principle, since it varies as well with the nature of the colouring matter as with the nature of the fibrous substance. An insoluble colouring matter can in no case be deposited alone on the fibre, for the least friction would cause it to become detached. When a very finely divided insoluble colouring matter is mixed with a solution of gum or gelatine, or any other viscous material, and is thus applied to a tissue, the thickener, when dry, will form upon the surface of the fibre a kind of varnish, which will cause the powder to adhere temporarily or until brought under the influence of water. Some kinds of mixed gauze tissues not intended to be washed are coloured in this manner-too often with poisonous compounds. Many of the finer tissues admit only of this method of colouring, instanced in the case of mixed raw silk and cotton fabrics. These fabrics are sometimes coloured with Scheele's green, and the colouring matter becomes detached by friction. It is evident that if any substance can be found possessing the property of glueing, as it were, the colouring matter to the woven tissue, then it is possible to fix colours otherwise insoluble in neutral solvents. Such a substance we possess in albumen, and from what has been said it will be readily understood that the property possessed by albumen of coagulating at a high temperature greatly enhances its practical value, because by its agency colours may be fixed under the action of steam.

If it is found desirable to fix to cloth any insoluble substance otherwise than by means of an agglutinative, it is then indispensable that it be first dissolved, in order that it may thoroughly penetrate the pores of the fibre and be uniformly divided. We have here to distinguish two cases which can occur—

r. The insoluble substance may be only very weakly retained in solution by its solvent, and the molecular attraction of the fibre may be stronger than that of the solvent menstruum. In this case there will be precipitation of the dissolved matter without any extraneous aid. This action is instanced with an alkaline solution of reduced indigo in which cotton is immersed; decomposition and precipitation take place, and the dissolved (white) indigo is attracted so strongly that the amount of indigo taken up increases with time. According to M. Persoz, a solution of alumina with excess of base cedes to cotton fibre its excess of alumina.

2. But if the affinity of the solvent for the dissolved matter be greater than that of the fibre it becomes necessary to employ means by which this resistance may be overcome, and the colour precipitated in an insoluble condition upon the fibre.

The explanations of the modes of action under these principles are very many and various. According to some, the fixation of the insoluble colouring matter is mechanical—the solid molecules being considered to have penetrated the pores of the fibre by endosmose, and by becoming precipitated to have lost their motive power. This theory, first promulgated by Hellot, le Pileur D'Apligny, and Macquer, has been urged with great ingenuity and talent by Mr. Walter Crum, with, however, essential modification of the erroneous views of the previous theory. According to others, who have at their head M. Chevreul, a true chemical combination takes place between the fibre and the colouring matter. It does not appear possible to assimilate the dyeing of cotton by means of indigo, oxide of iron, or oxide of chromium, &c., with a chemical phenomenon of the same order as the union of oxygen and hydrogen, of sulphur and iron, which takes place in definite atomic proportions, and after which the constituents have entirely or partially lost their distinctive individual characters. It is true there exists for the fibre a state of saturation beyond which it is not capable of retaining a further quantity of colouring matter; but there does not appear to exist between the quantity of fibrous matter and of colouring matter any atomic or relative proportion. On the other hand, neither fibre nor colour loses after fixation any single distinctive quality that it before possessed.

The colouring matter can be removed from the fibre to which it has been fixed by any solvent which would act upon it in its free state, leaving the fibre perfectly intact. This would show at most only a molecular attraction similar to that exhibited by carbon and many other porous bodies. Should it be urged that the precipitation of indigo or of basic alumina is evidence that there exists in cloth fibre a chemical affinity capable of overpowering another similar affinity, it may be answered that the force of diffusion alone is capable of determining the dissociation of compounds, the elements of which exert powerful mutual attraction. For an instance may be cited the combination of sulphuric acid and sulphate of potash in the bisulphate of that base.

Summing up our evidence, it appears that the fixing of colouring matters and insoluble substances upon fibre may be best considered from the point of view taken by Mr. Walter Crum. It may be added that molecular attraction aids permanent adhesion. The theories propounded by M. Persoz and Mr. Walter Crum are not diametrically opposed, as would appear at first sight; indeed, it might be urged that their views are compatible. The essential

difference may be thus shortly stated. M. Persoz holds that the colour is fixed to the surface only of the fibre; Mr. Walter Crum thinks the fibre to be perfectly permeated by the colour. No other portion of our subject is so difficult as the one upon which we are now engaged, and none so little remunerative, for were our knowledge precise and complete upon this point the gain would not be great.

The practical view of the question leads to the following considerations:-A mordant is a substance which can exert an affinity for the fibrous material to which it is applied, at the same time possessing an attraction for colouring matters. Mordants are not very numerous, and the class may be subdivided into mordants proper and mordants of a dubious nature. The first division contains those metallic salts whose oxides appear to effect an intimate chemical union with the fibre and colouring matter. The second division includes a number of substances, which, possessing some affinity for colouring matter, do not appear to combine with the cloth in a chemical, but rather to adhere to it in a mechanical manner. Under the first division may be mentioned the so-called mineral mordants, salts of iron, zinc, alumina, tin, and copper; to the second division belong some vegetable and animal matters, as galls, oils, albumen, caseine. With wool, silk, hair, skin, horn, and bone there exists naturally an affinity for colouring matters, but not to an extent sufficient to yield general good results. There are only a few colours that can combine with either vegetable or animal tissues without the aid of a mordant, and of these the majority are much improved both in brilliancy and fastness by the presence of a mordant. The colouring matters of madder, logwood, fustic, and many other dyes are by themselves capable of imparting a feeble colour to unmordanted calico, but with the assistance of mordants they communicate fast and brilliant hues. Although several colouring matters can impart their shade to woollen fabrics without a mordant the hue is poor and feeble, lacking lustre, and not possessed of any great stability. The colouring matters of indigo, safflower, and annatto impart colour to cotton fabrics without the agency of a mordant, which does not much improve the depth and colour; and for woollen tissues may be added picric acid, archil, and many of the aniline colours. Silk behaves very similarly to wool, and with the exception of indigo-a dye sui generis-all the colours are loose and unstable. There are certain conditions absolutely necessary to the constitution of a true mordant. The first is solubility. Unless the metallic oxide to be used as a mordant can thoroughly permeate the fibres, the colour will not resist washing, at least with soap and hot water; and such complete permeation cannot take place except the mordant be in the condition of a clear solution. The property of becoming insoluble is the second essential of a mordant; it is apparent that if a mordant be carried into the pores of the fibre simply on account of its solubility, that the same reason would cause its return, unless means were taken to fix it permanently upon the spot to which it has penetrated. This insolubility is obtained in various ways. The metallic oxide is combined with a volatile acid, such as acetic acid, which, after volatilisation, leaves the oxide insolubly fixed in the fibre; this method is most generally employed. Or the oxide may be combined with a non-volatile acid, the acid being removed by ' chemical means, such as an alkaline bath, exposure to vapours of ammonia,

&c. In the case of nitrate of iron, a salt is chosen which holds one part of its oxide in a comparatively loose state, and, when diluted with water, allows the feeble affinity of the fibre to remove it from the acid. A similar process takes place with alum when a portion of the acid has been removed by salts having an alkaline reaction.

The vegetable and animal mordants differ in their method of adhering to the fibre. Oil, as employed in Turkey-red dyeing, undergoes a change by exposure to the air, which renders it insoluble and irremovable by ordinary agents. Albumen and similar substances possess a mechanical affinity for the cloth; they are applied in the soluble state, and become insoluble by heat, or some other agent which coagulates them. They embrace the fabric in a reticulation of fibres, and may be considered as rather holding to the surface than as retained in the interior of the fibre.

There now arises the question, what is the nature of the combination which takes place between the mordant and the fibre? No direct nor positive answer can be given, for the question is involved in doubt and controversy. while the evidence on the various views is so inconclusive that no satisfactory result can be arrived at. The insoluble particles of the mordant may be retained simply in a mechanical manner by the fibre, which is supposed to be hollow, and to act the part of a trap; or the fibres may be porous, and the acid solutions penetrating the pores leave their oxides in contact with the walls of the cells, from which they cannot escape, either by reason of the narrowness of the cells or some supposed conformation of the metallic oxide. The mordants, again, separated by more powerful chemical agents, or through destruction by time, may form a chemical combination with the matter of the fibre. Or the fibre may possess some active power of adhesion on its exterior walls for the metallic oxides, and they may be held together by virtue of the power of contact. All these theories are held, and the sum of the evidence that can be drawn from chemical or microscopical observations does not bear more on one side than on the other. In the absence of any satisfactory scientific account, we may undertake the practical supposition that the particles of mordants are held by the fibres in a state of chemical freedom, capable of exerting all their affinities, and drawing to themselves those substances for which they have an attraction.

The affinity which the mordants have for the colouring matter is undoubtedly of a chemical nature. A given quantity or strength of mordant can combine with only a certain amount of colouring matter to produce a certain shade, and, as is the case in most chemical combinations, the colour of the resulting compounds bears no necessary resemblance to that of the constituents. The shades of colour which any dye-stuff can give differ for each mordant, and for various strengths of the same mordant. The same colouring matter will yield shades that appear quite opposite in their nature, as, for instance, madder, which with weak alumina mordants gives pink, with strong red; with weak iron mordants, lilac or violet, with strong black colours; while a mixture of iron and alumina mordants yields various shades of chocolate.

A given mordant has not the same properties upon all kinds of fibre. Tin mordant, so extensively employed in woollen dyeing, and yielding fast colours, is a very feeble mordant on cotton, and never gives colours comparable for

fastness with those of alumina or iron. On the contrary, iron mordants are very difficult to employ on woollen fabrics.

A mordant may be applied to a cloth in three ways with regard to the colouring matter:—

r. The mordant may be applied before the colouring matter; and this is usually the case in calico printing, for dyed goods, and frequently in piece dyeing.

2. The mordant may be applied after the colouring; this process is generally adopted in piece dyeing, where the pieces are first passed through the extract of the colouring matter, and then through the metallic mordant.

3. The mordant and colouring matter may be applied simultaneously; this takes place with many colours in dyeing, and with all steam and spirit colours in calico printing.

In the first case, where the mordant is applied before the colouring matter, the method is necessary in printing designs upon the fabric to be dyed. It is essential that the mordant should be thoroughly fixed upon the cloth before passing the latter into the dye-beck, because a design requires that there should be at least two shades of colour, one of which may be the white of the cloth, and it is to be easily conceived that if the mordant were loose or floating about in the dye-beck it would attach itself indiscriminately to all parts and destroy the design. The fixing of the mordant necessitates several processes unknown in piece dyeing.

In the second case, that of applying the colouring matter before the mordant, the method is employed with only self-coloured fabrics, and has arisen from motives of convenience and economy. It usually happens that the mordant is much cheaper than the colouring matter in regard to the quantities employed, and the colouring matter can be more completely utilised by having the mordant in excess.

The method of using the mordant and colouring matter together is one of limited application, because in the majority of cases insoluble lakes are formed, not well adapted to give good and fast colours. In calico printing it is possible to use the colouring matter in a concentrated state and in combination with acids and other matters, which keep it and the mordant in a state of solution until the affinities of the cloth come into play, assisted also by artificial means, as steaming, passing through alkaline baths, &c., to cause the formation of an insoluble compound and the adhesion of both mordant and colouring principle to the cloth.

In practice, colouring matters are classed according to the process by which they are fixed, as—dye colours, steam colours, and colours otherwise applied. This classification is arbitrary and vague. The following classification, although it possesses but few chances of general acceptance in practice, has the advantage of being rational:—

A. Mechanical fixation of insoluble colours.

An insoluble colouring-matter is applied in the state of a very finely divided powder, and is fixed upon the fabric by means of a substance which becomes solid and generally at the same time insoluble. Examples are given in the dyeing of tissues with ultramarine, Guignet's green, and lamp-black, fixed by means of albumen, gluten, caseine, or shellac.

B. The colouring matter combines with the fibre; the colour is the result of this union.

This simple dyeing may be subdivided into:-

- a. The woven fabric or fibre is immersed in a bath or solution of colouring matter at the ordinary, or at a higher, temperature. The fabric gradually draws the colouring matter from the bath by a true chemical attraction. In this manner a uniform colour is imparted to the whole tissue, unless a resist had previously been printed on; or, the uniform colour is subsequently discharged in certain patterns by means of acids and other reagents. Examples: The dyeing of woollen and silken fabrics with aniline colours, sulphindigotic acid, picric acid, orceine. Vegetable fibre cannot be dyed by this method.
- B. The colouring matter is printed on the cloth after mixture with a thickener, and the colour is subsequently developed by exposure to the heat of steam.
- C. The colouring matter becomes incorporated, but not chemically combined, with the fibre.
 - I. The fixation of colour by surface attraction at the moment of separation from the solvent, as with carthamine; or precipitation due to the action of porosity and surface attraction upon a colour which is only feebly united to a solvent, as with indigo, annatto, &c.*
 - II. Fixing colouring matter properly dissolved by means of the chemical attraction exerted by a previously mordanted fibre. The difference between this method and that described under B is, that in consequence of the absence of any affinity between the colouring matter and the fibre, the latter has been prepared or provided with an insoluble substance, which possesses the power of combining with the colouring matter, and of fixing it firmly to the fibre. Mordants do not act in this manner only, but exercise as well the function of varying and regulating the shade and the depth of colour. For example, when non-mordanted wool is steeped in a solution of cochineal, it will assume a claret-red or a grenadine-red colour; but if the wool has previously been mordanted, it will assume a bright scarlet. Cotton fabrics previously mordanted with iron or alumina mordants will, on immersion in a madder bath, exhibit a violet, black, red, pink, or chocolate colour, according to the nature of the mordant and its strength.
 - III. Fixing by oxidation. The colouring matter, or rather the matter capable of development as a colour, is applied to the fibre in solution (either by immersion or by printing), and is next submitted to an oxidation which precipitates or fixes and as well developes the colours. Examples: the fixing of catechu, logwood, aniline black. The oxidation is induced
 - a. By exposure to air, with or without addition of any alkaline substance.

^{*} The development of the colour requires, in the first instance, a subsequent oxidation, which does not, however, render the colour more durable, nor prevent re-solution in any menstruum similar to that of the first solvent.

- b. By passing the tissue through any bath or solution containing an oxidising material, such as a chromate.
- c. By the introduction into the colouring mixture which is to be printed on the cloth of some oxidising substance, which on exposure to an elevated temperature gives off oxygen.
- IV. The colour is dissolved in a suitable solvent, which is capable of being volatilised by exposure to air and heat. This method is employed in the fixing of the acetates of iron and alumina, for example, and is sometimes accompanied by oxidation. Steam-heat is generally used to effect the volatilisation.
- V. The colour is formed upon the fibre by double decomposition or displacement effected by means of two salts, or a salt and an alkaline hydrate, or an alkaline carbonate. One of these compounds is applied to the fibre in solution, while the other is dissolved in a suitable fluid, and the fibrous material is passed through this solution. Examples: fixing the oxides of iron, chromium, copper, manganese, &c. This process also serves for the fixing of certain mordants, and is employed in many cases with acetate of alumina mordants in conjunction with the dung-bath. Oxidation is sometimes necessary at a subsequent stage for the development of the colour.
- VI. The constituent elements of a colour are presented to the fibre in solution by chemical means, and in such a manner that—either under the subsequent influence of moisture and heat or by lapse of time—they unite to form an insoluble and adhesive colour. Under this head may be included the dissociation of the ferro- and ferricyanhydric acids by the influence of heat; the result of such dissociation is subsequently oxidised to obtain a deposit of Prussian blue

Notwithstanding the many subdivisions of our classification, there are some cases to which it is not applicable. To these belong those instances of multiple reactions, or of special agency, which will need presently a more detailed treatment.

The colouring materials which we shall pass in review may be divided into two groups, viz.—

Mineral Products, and Organic Substances.

Among the members of the latter group we shall meet with a large number of substances of vegetable and animal origin which have not been reproduced artificially, and the constitution of which is imperfectly known, exhibiting no other relation than that of similarity in colour. Others, again, have been reproduced artificially, and are chemically well defined.

CHAPTER II.

MINERAL PIGMENTS.

WE shall under this head have occasion to revert to some mineral salts, which we have treated elsewhere with other views; the re-statement here is necessary when we specially regard the mineral as a pigment.

Every mineral colouring matter that is insoluble in water, and reduced to an impalpable powder, can be applied to woven tissues by means of plastic substances, such as albumen. Every mineral colouring matter insoluble in water, and capable of development upon textile fabrics by soluble substances (that is to say, by precipitation), can be employed in the processes of dyeing and printing. Practically, however, the number of mineral pigments is limited. Various reasons can be given for the large number of exceptions. Leaving out of consideration the question of cost, there are such desiderata as brilliancy, resistance to the influence of light, atmospheric and chemical action, difficulties in fixing certain colours, and, finally, the danger of poisoning as a consequence of the use of certain pigments. As mineral colours vary largely in composition and character, it will be unsatisfactory to give a general review of their properties, but will be better to treat them specifically. As to classification, the pigments may be separated into as many divisions as there are colours in the spectrum, and further into groups according to their chemical relations. The means and methods employed in fixing these materials upon woven tissue will be separately described for each particular substance.

WHITE COLOURING MATTERS.

To these belong, in a very limited sense,-

Chalk, or Carbonate of Lime.

Used as an oil-paint for in-door work, and as a water-colour when mixed with gelatine. Chalk is sometimes employed to dilute other pigments,—that is to say, to modify the shade, as with chrome-yellow and orange, ultramarine, and Brunswick green. Prepared chalk is used in manufacturing chemistry for the purposes of saturating acid fluids. It is not used as a pigment in dyeing or printing.

Sulphate of Lime, or Gypsum.

Perfectly white plaster-of-paris (so called because the geological formation upon which Paris stands is very rich in gypsum) is of only limited use as a paint in the manufacture of paper-hangings, being then mixed with gum-water. It is not employed as an oil-colour, and does not find any application in pigment-printing.

Sulphate of Baryta.

This is a widely distributed mineral, and often occurs in a perfectly pure white state. It is, for all practical purposes, insoluble in water and acids, and is not acted upon by sulphurous emanations. In hue it is of dazzling whiteness, especially when amorphous. It is a perfectly innocuous pigment. Its great defect is that it covers badly; in order to reduce to a lighter shade of blue a certain weight of ultramarine, one part of white-lead has the same effect as 5 parts of powdered native sulphate of baryta. The artificial sulphate, especially that prepared by M. Kuhlmann's method, covers very well, being obtained in an amorphous state. Chemists know that when sulphate of baryta is precipitated from hot, and not too concentrated, solutions, it assumes a crystalline appearance, and admits more readily of filtration. White-lead, neutral carbonate of lead, also covers badly, as a consequence of its crystalline condition, whereas the white-lead of commerce, being a basic carbonate, is purposely prepared in an amorphous state. It is the state of aggregation, not the chemical composition, which influences what is termed "covering power." Sulphate of baryta is not used as a pigment, except for reducing the shade of other colours. White native substances, as pipe-clay, kaolin, and similar aluminous minerals, and magnesian minerals, are not used as pigment colours.

We have already referred to the use of aluminous and magnesian minerals as thickeners, and it may be stated, in passu, that French chalk—chiefly a silicate of magnesia—is employed in dressing and finishing calicoer. Zinc-white, anhydrous oxide of zinc, is occasionally used in pigment-printing, not, however, by itself, but as a diluent to reduce the depth of shade of high- or dark-coloured pigments.

Among the substances applied to woven tissues, by the same or similar means as pigment colours, should be mentioned the two metals, silver and tin. The former is employed as silver-leaf, but, on account of its extraordinary sensitiveness to the action of sulphurous emanations, the other metal, tin, is preferred. Tin prepared in a very finely divided state is known commercially as argentine, and is obtained in this form by precipitation of a slightly acid solution of one of its protoxide salts by means of zinc. The tin solution should be very dilute, and only very slightly acid; the quantity treated at one operation should be comparatively small. The following arrangement is often employed: - Into cylindrical vessels of glazed earthenware, capable of holding 12 litres (21 gals.) each, is poured 8 to 10 litres (11 to 2 gals.) of solution of chloride of zinc at 10° to 15° Baumé, to which is added 4 to 7 grms. (62 to 108 grs.) of tin-salt, known as crystals of tin, protochloride of tin. Pieces of sheet zinc are then placed in the vessels, and when the reaction has ceased the fluid and the precipitated metal are poured upon a clean silken sieve. To the filtrate tin-salt is again added, and the operation repeated. The precipitated metal is collected upon a filter, washed with water, dried at a gentle heat, and passed through a fine silken sieve, to separate the most finely divided metal. The metal is applied to the woven tissue by mixing about 360 grms. (5544 grs.) with a litre of an ammoniacal solution of caseine. The printing is effected by blocks or rollers, and a metallic lustre is developed by heavy calendering and hot-pressing machines. Argentine effects have

also been produced by a totally different process. Solutions of the more easily reducible metals, such as silver, lead, tin, bismuth, &c., free from excess of acid, were mixed with suitable reducing agents, such as aldehyde, methylic spirit, and thickened with glucose. This mixture being printed upon the fabric, a pattern was brought out in reduced metal. The ease with which such delicate metallic films were acted on by sulphurous fumes present in the atmosphere caused the goods soon to become very unsightly, as the process is, for the present, in abeyance. It so happens that with the exception of gold, which is too costly for articles of common consumption, the more readily reducible metals have all a strong affinity for sulphur, by which they are blackened. A practicable method of depositing, e.g., aluminium upon silk or worsted goods, would be of great value.

RED MINERAL PIGMENTS.

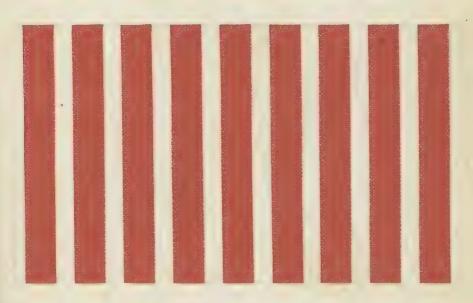
Of red pigments minerals yield—one iodide, that of mercury; three sulphides, viz., cinnabar or vermillion, the sulphide of mercury,—antimonial vermillion, the tersulphuret of antimony,—and realgar, or the bisulphide of arsenic. Among the oxides and derivatives we have—red-lead, or minium, a peculiar oxide of lead; English red peroxide of iron, red ochre; suboxide of copper; the red oxide of tin, a modification of oxide of tin; purple of Cassius; chromates of mercury and silver; and subchromate of lead. None of these or any other red mineral pigments are suitable for use on the large scale, owing to their high price, and in some instances to the fact that they have a great tendency to subside from the fluid in which they are suspended.

Bi-iodide of mercury yields a very rich scarlet, easily formed by the union of iodine and mercury, or by double decomposition between a soluble iodide and a solution of corrosive sublimate. 200 grms. of mercury are triturated with 254 grms. of iodine, with the addition of a little alcohol; or a solution of corrosive sublimate is precipitated with iodide of potassium, or, more economically, with iodide of iron produced by the action of iron on iodine in the presence of water.

The fixation of the colouring matter upon cotton tissues is a simple operation, but as the colour is very fugitive it is in very little request.

Cinnabar, vermillion, or sulphide of mercury, is formed artificially by a dry or wet process, but a cinnabar which occurred native was known in Pliny's time by the term minium. In the former process, 540 parts of mercury and 75 parts of sulphur are intimately combined to form a black powder, which is introduced into iron vessels, and exposed to sufficient heat to fuse the mass. The fused mass, when cool, is broken up, and introduced into loosely-covered earthenware vessels, heated on sand-baths; when sublimed the mass is pulverised, the result being a powder of a cochineal-red colour. Vermillion is obtained by the wet process, by precipitating a solution of corrosive sublimate in ammonia with a solution of sulphur in sulphide of ammonium; or, according to Dr. Von Martius, by agitating I part of sulphur, 7 parts of mercury, and 2 to 3 parts of a concentrated solution of liver of sulphur. M. Brunner prepares a vermillion of the highest order of brilliancy by mixing 114 parts by weight of sulphur and 300 parts by weight of mercury, with the addition of a small quantity of caustic potash solution. This mixture is then treated with a solution of 75 parts caustic potassa in 400 parts of water, and heated on a water-bath to about 45° C. After some hours the mixture acquires a scarlet colour, and is then collected on filters, washed, and dried. The dried powder is the vermillion of commerce.

The annexed specimen of vermillion-red we owe to the kindness of Mr. Walter Crum, of the Thorniebank Print Works, Glasgow. It is produced by the following process:—5 lbs. of vermillion are mixed with I gallon of thickening; the colour is then printed on the fabric, which is dried and steamed for one hour. The thickening consists of a mixture of solutions of gum-dragon and egg-albumen. These may be in different proportions, according to the degree of fastness required. The more albumen used the faster will be any pigment or paint colour. The gum-dragon solution is used in the proportion of ½ to ¾ lb. per gallon of colour, and the albumen to the amount of 4 lbs. in the gallon of colour: these proportions yield the fastest colour that is prepared. 2 lbs. of albumen will give a moderately fast colour.



VERMILLION RED.

Oxysulphuret of antimony, antimony cinnabar, or antimony vermillion, is a similar compound to vermillion. It may be prepared on the large scale by the following process:—Black sulphuret of antimony is calcined in a current of air and steam, with the view of forming antimonic oxide and sulphurous acid, the latter being employed for the preparation of dithionite of calcium from soda-waste. The antimonic oxide is dissolved in hydrochloric acid. Large wooden vessels, heated by steam-pipes, are nearly filled with a solution of dithionite of calcium, and the protochloride of antimony is added gradually, the liquid being stirred and heated to about 60° C. After the reaction has ceased and the precipitate subsided, the latter is washed and dried at a temperature under 50° C. Mixed with water or a solution of gum, the colour appears very dull; but as an oil-colour it possesses the most intense brilliancy. Recipes for its application to printing have not been given.

Of the other red pigments, of very limited application in printing, we need not speak in detail.

YELLOW MINERAL PIGMENTS.

Of these we have the following:—Two iodides; that of lead and the yellow iodide of mercury. Sulphides: orpiment, a peculiar sulphide of arsenic; sulphide of cadmium; the yellow-orange sulphide of antimony; and bisulphide of tin. Oxides: hydrated oxide of tin; crocus martis, a yellow hydrated oxide of iron; massicot, oxide of lead; and oxide of uranium. Salts: Naples' yellow, an antimoniate of lead; uranates of soda and potash; the insoluble chromates of lead, bismuth, zinc, baryta, strontia, and lime; Cassel yellow, an oxychloride of lead; antimony yellow, an intimate mixture of the oxychlorides of lead and bismuth and of antimoniate of lead. Metals: gold; and so-called Dutch gold, an alloy of copper and zinc and of copper and tin, manufactured chiefly at Nuremberg, in Bavaria.

This list contains a large number of mineral yellows employed exclusively as oil-paints; others may be fixed to woven tissues by the aid of plastic substances; and, finally, the list includes the peculiar class of colours which admit of direct precipitation upon the fabric. These are the insoluble chrome colours, produced by an application, first, of subacetate of lead, and subsequent immersion in a bath of neutral chromate of potash.

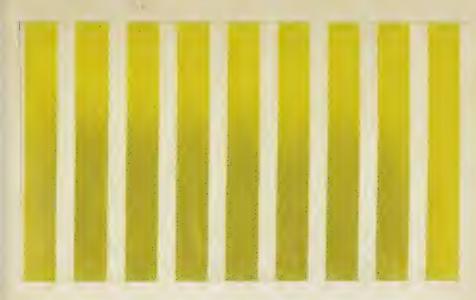
In the year 1820 the use of chromate colours was first attempted by M. Lassainger. He steeped skeins of prepared or de-gummed silk in a weak solution of subacetate of lead for about two hours. The silk was then washed in clean cold water, and immersed in a dilute solution of neutral chromate of potash. Upon this principle is based the application of the soluble chromates in dyeing and calico printing. These colours are readily detected by their property of becoming tinged a deeper orange by the action of ammonia and of lime water, while acetic or citric acids restore the yellow colour. Alkalies and strong hydrochloric acid permanently destroy these colours.

The subjoined specimen of chrome-yellow or canary-yellow, printed upon cotton by Messrs. Walter Crum and Co., is an illustration of the use of chromate of lead. The colour is produced upon the cloth by the following process:—24 ozs. of white sugar of lead are dissolved in each gallon of water, and thickened with 4 lbs. of British gum. This solution is printed on to the cloth, which is then dried and passed for two minutes through a cold bath of bichromate of potash and common salt containing 6 ozs. of bichrome and 24 ozs. of salt to the gallon. The cloth is finally well washed and dried.

Another shade of yellow may be obtained on yarn by a treatment which is chemically the same. 25 lbs. of cotton yarn are run through a bath of 2 lbs. of sugar of lead for twenty minutes; then through a weak lime water bath. The yarn is removed from the lime bath at the end of five minutes, wrung out, and passed through a cold bath of 1 lb. of bichromate of potash and 1 lb. of hydrochloric acid.

If buff may be considered a shade of yellow, we may here detail how the colour known commercially as *iron-buff* is produced. This colour is illustrated in the subjoined specimen of printed cloth, likewise obtained from the same distinguished firm.

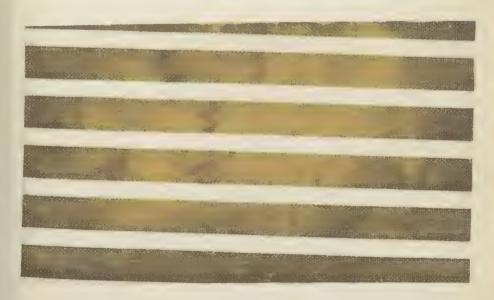
There is first prepared a "standard liquor," from which in several proportions with the thickening almost as many shades can be obtained. 4 lbs. of copperas or sulphate of iron are dissolved in each gallon of water, to which



CHROME- OR CANARY-YELLOW.

are added 2 lbs. of acetate of lead, the mixture being stirred until solution is complete. The deposit is allowed to subside, and the clear liquor, which should stand at 27° Tw., strained off. This standard liquor is, in the shade given in the specimen, mixed in the proportion of 1 measure (at 27° Tw.), to 3 measures of a solution of gum substitute at 5 lbs. to a gallon. The mixture is printed on the cloth, which is dried, and the colour is raised (or developed) by passing the fabric through a cold solution of soda-ash at 12° Tw. for two minutes, when it is rinsed in water, washed, dried, and passed through a weak solution of chloride of lime by the mangle, and again dried.

This colour is also known under the term of "rust" yellow. A darker shade of rust-yellow generally used for warps for goods which are to be coloured Prussian blue, may be coloured in the yarn by the following method:—25 lbs. of clean cotton yarn are run through a bath of 3 lbs. of copperas



IRON-BUFF.

and 2 lbs. of nitrate of iron for about five turns, and are wrung out. The yarn is next taken through a strained cold bath of 4 lbs. of lime for five turns, and the colour is submitted to oxidation in the air. When even, the yarn is again dipped in the iron bath and again in the lime, and oxidised until the desired shade is obtained. The colour is fast.

Gold leaf, pure or alloyed, or imitation, is applied to woven tissue by means of albumen or a fatty and resinous mordant.

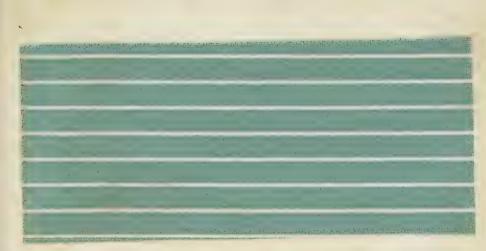
GREEN MINERAL PIGMENTS.

Mineral greens may be divided into two groups. To the first belong those mineral compounds possessing a green colour and well-defined chemical constitution, as chrome-green or hydrated oxide of chromium; Scheele's green or arsenite of copper; Schweinfürt green or aceto-arsenite of copper; and the emerald greens. The second group includes all those various shades of green which are composed of mixtures of blue and yellow pigments, and constitute simply mechanical mixtures.

The larger proportion of green pigments belonging to the first group are preparations derived from chromium and copper, to which may be added Rinmann's green, a compound of cobalt and zinc, Rosenstiehl green or manganate of baryta, green ultramarine, and some green prussiates. As Guignet's green, a chrome-green, is extensively used, it may be interesting to know how it is produced. Three parts of boracic acid are intimately mixed with one part of bichromate of potash and a sufficient quantity of water to form a thick paste. The paste is introduced into a furnace and heated to a dull red heat, when a borate of potash and a borate of oxide of chromium are produced. The mass is allowed to cool, and is then thrown into cold water; the borate of potash is dissolved, and the borate of chromium is decomposed; the hydrate of the oxide of the metal C2O3+3HO subsiding as a magnificent green powder, which only requires to be well washed and drained to be ready for use. This green and that prepared from phosphate of ammonia and bichromate of potash possess the property of maintaining their colour by artificial light.

Chrome-green, like other pigment colours, is fixed either with lactarine, or with albumen thickened with gum or starch. In either case the cloth is subsequently steamed.

Among the preparations of copper that possess a green colour only a few are employed in dyeing and printing. The principal are—Arsenite of copper, termed Scheele's green, and designated by as various names as their places of manufacture, is a compound the constitution of which is expressed by the formula As₂O₄Cu"_{II}. This pigment may readily be fixed to tissues by first passing them through a solution of a salt of copper, then through a solution of arsenious acid. A more expeditious method consists in passing the fabric through a bath of arsenite of soda, and then through a solution of a salt of copper, generally the sulphate. The accompanying specimen of printed cloth, from the firm of Messrs. Wood and Wright, coloured with Wilner green, by an arsenical process, illustrates the application of this class of pigment colours. The process is as follows:—4 lbs. of sulphate of copper are dissolved in I gallon of hot water, and the solution is



CHROME-GREEN.

thickened with I gallon of gum tragacanth water. The solution when strained and well mixed is ready for printing. When printed, the cloth is passed on rollers through a solution of arsenite of soda at 6° Tw., each length of cloth being about 15 seconds in the bath. The fabric is then rinsed in cold water, dried, and finished.

The arsenite of soda bath is prepared by dissolving two drams of white arsenious acid in r gallon of caustic soda at 5° Tw. If a deeper yellow shade should be desired, more arsenic must be employed; if a deeper shade of blue, more soda. By varying these constituents several shades of green may be obtained.

Aceto-arsenite of copper,—

Wilner, an Arsenical, Green.

is, when used, fixed by means of albumen, but may be fixed chemically by printing on a mixture of acetate of copper and arsenious acid, and steaming; or by rinsing the fabric previously treated with arsenite of copper through a bath of acetic acid.

The colours derived from insoluble salts of chromium are numerous, and although with the present valuable innovation of aniline dyes it is improbable that chrome or mineral pigments will meet with greatly extended application, we may shortly review the characteristics of the principal green pigments.

Arnaudon green, or netaphosphate of chromium, is a very similar colour to Schweinfurt green, but less vivid. According to M. Arnaudon it is best prepared by mixing equivilent parts of neutral phosphate of ammonia and of bichromate of potassiun (128 parts of phosphate and 149 parts of bichromate). The salts are pulverised together or dissolved simultaneously in a very little water, and the liquid is evaporated until it can be removed in the mass on cooling. The product is placed in a vessel, and heated upon an oil-bath to 180°. Should the temperature rise beyond 200° the green colour will have disappeared. The result of this process is washed in water, leaving a fine powder of a colour approaching that of budding leaves. The loss of colour at too high a temperature is probably due to the reduction of the bichromate in excess by the ammonia of the phosphate.

Plessy green is obtained, according to the inventor, by dissolving 1 part of bichromate of potassiun in 10 parts of boiling water, and throwing in 3 litres of biphosphate of lime and 1.25 kilos. of powdered sugar. A large quantity of gas is quickly disengaged, and when the action is no longer apparent the liquid is decanted, and the precipitate washed in water.

This green does not suffer alteration by exposure to the action of the air, or of sulphuretted hydrogen. For printing this colour is too pale, but it has met with several applications.

BLUE AND VIOLET PIGMENTS.

Blue and violet pignents include ultramarine, the blue colours derived from cyanogen and ferro-cyanogen compounds, cobalt blue, Thenard blue, smalt, phosphate of cobalt (cruleum, the blue oxides of some of the rarer metals, as for instance, molybeenum blue, tungsten blue, and a few others.

Ultramarine.

The artificial production of this magnificent pigment is one of the greatest conquests of modern chemistry, and is due entirely to the labours of Messrs. Guimet and Gmelin, working, however, independently of each other. The mineral known by several names, but generally called lapis lazuli, or simply lapis, is one of the rather rare substances found disseminated through a peculiar kind of granice, especially in Central Asia. Although it was known in Europe as far back is the times of Raphael and Michel-Angelo (both these artists employed it), its true composition remained a secret until the beginning of this century; but it is from the results of the quantitative analysis of this mineral that the manufacture of artificial ultramarine has taken its origin. The characteristic difference between native and artificial ultramarine is that the native pigment, as obtained by lixiviation of the pulverised mineral, is not acted upon by strong or distilled vinegar, nor by a concentrated solution

of allum in water, both of which discolour and decompose artificial ultra-

In the year 1814 M. Tassant accidentally observed he formation of a blue-coloured substance in the soda furnace at St. Gobain. The substance having been submitted for analysis to Vauquelin, he found it to be identical in composition with lapis lazuli, and thence argued the possibility of its synthesis. In the year 1824 the Société d'Encouragement pour l'Industrie Nationale offered a prize of 6000 francs (£240) for the discovery of a practical method for the preparation of ultramarine by artificial means, it a price not exceeding 600 francs the kilo. In the year 1827 M. Guimet annunced to the Académie des Sciences that he had succeeded in solving the proilem of the manufacture of this substance. The discoverer established a manufactory near Lyons, and lhad for many years the monopoly of the trade, though the price of 600 francs (£24) per kilo. sank to 30 francs. The then Professor of Chemistry at Tübimgen, M. C. Gmelin, claimed priority of discovery; but after a lengthy, impartial, and painstaking inquiry, there remained no loubt whatever that M. Guimet had claim to the premiums offered.

The manufacture of ultramarine is carried on in France and some parts of Germany along the Rhine, and in Bavaria. The process there in use was, however, imported from France.

The trade distinguishes four kinds of ultramarine, vz.—(1). The deep and pure blue, as to its colour quite identical with the average of native ultramarine. (2). Pale blue ultramarine, sometimes with a green tinge, but always a very brilliant pigment. (3). Ultramarines of a violet it rose hue. (4). Green ultramarine, of a dull appearance. As many as thirty-ix different varieties of ultramarine, gradually verging from perfectly pure blue to pure green, may be met with.

Ultramarine, artificial as well as native, is decomposed by excess of hydrochloric acid; sulphuretted hydrogen is given off, leaving a milky and gelatinous liquid, which runs turbid through filtering-paper, oving to the very finely divided state of the sulphur, the quantity of which is far larger in artificial ultramarine than in the native product. Ultramarine is not affected by air and sun-light, withstands washing with soap and alkalis, and is fixed upon tissues by means of albumen. There exists no prod whatever as to the origin of the blue colour of this pigment. Notwithstanding the number of analysies made of the native as well as of the artificial product, no rationale can be given of the blue colouration from the composition of the material, while the question arises whether or not the component substances are modified as soom as acids are caused to act upon them.

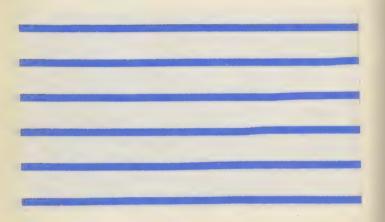
The manufacture of ultramarine on the large scale requires a great deal of skilful management, and more than ordinary tact, in regulating the heat, which is always higher than full red-heat. The material callet green ultramarine is the result of incomplete ignition.

Ultramarine is a substance not subject to wilful adulteration to any great extent; it is sometimes customary to dilute the pigment with whites, such as sulphate of baryta and lime. Ultramarine of good quality exhibits an extremely deep blue powder, which imparts its beautiful colour very readily to other substances with which it is mixed. It is used inprinting, and is fixed by means of albumen and steam.

We append a sample of cloth dyed with this colour by the firm of Messrs. Walter Crum and Co.

To fix this colour, the goods, after printing, are steamed for half to one hour.

The raw materials for the manufacture of artificial ultramarine are—
(1). Silicate of alumina, as free as possible from iron, the kaolin of Cornwall being preferred. (2). Calcined sulphate of soda. (3). Calcined soda. (4). Sulphuret of sodium, a by-product of the manufacture. (5). Sulphur. (6). Pulverised coal or charcoal. The clay is washed with water, dried, ignited, and ground to a very fine powder. The sulphate of soda must be free from lead or iron. Potassium salts will not form ultramarine; barium salts have the property (see "Chemical News," vol. xxiii., pp. 119, 142, 204). Alkali works supply the calcined soda, which should contain at least 85 per



ULTRAMARINE.

cent of carbonate of soda. Caustic soda may be substituted. The sulphur and the carbon are both very finely pulverised.

There are three methods of preparing ultramarine generally followed: they result in—

- a. Sulphate-ultramarine;
- β . Soda-ultramarine;
- y. Silica-ultramarine.
- a. The preparation of sulphate ultramarine is included in two stages:
 - 1. Preparation of green ultramarine.
 - 2. Conversion into blue ultramarine.
- (1). The kaolin, sulphate of soda, and charcoal are all finely pulverised; or if solutions of sulphate of soda, soda, and sulphide of sodium are used instead of powders, the kaolin is stirred with the solution, and the mixture evaporated to dryness and ignited. The materials are employed in such quantity that the soda shall saturate half the silica of the kaolin, and shall be present in

sufficient quantity to form with the sulphur polysulphuret of sodium. This and the formation of another sulphuret (Na₂S) are obtained by observing the following proportions:—

Dry kaolin			• •	100	100
Calcined Glauber's salt				41	83100
Calcined soda	9 10	0 0		41	
Charcoal or pit-coal				17	17
Sulphur				13	

This mixture is ignited without access of air, and a white mass is obtained, which becomes green by exposure to air, and blue by being calcined in contact with air. The mixture is placed in fire-clay crucibles, and well rammed down, the crucibles being maintained at a high temperature, with a limited supply of air for eight to ten hours, the ignition being completed at a white heat. The crucibles when cooled are found to contain a semi-fused grey- or yellow-green mass, which is repeatedly lixiviated with water. The green ultramarine contains, according to Stölzell's analysis (1855), in 100 parts—

raing to b	COLLO.		wiiwi)	010	(10)	1/9 ***	200	Pare	~	
Alumina										30.11
Iron										0.49
Calcium										0.45
Sodium	* *									19.09
Silica		• •				• •				37.46
Sulphuric	acid									0.76
Sulphur				• •						6.08
Chlorine					• •		• •		4 4	0.32
Magnesia,	, pota	ısh,	phos	pho	ric ac	cid				traces
										94.81
Oxygen						* *				2.10
										100,00

2. The conversion of green into blue ultramarine is effected by roasting the green ultramarine and sulphur at a low temperature, with access of air. Sulphurous acid is formed, a portion of the sodium oxidised into soluble sulphate being washed out; the sulphur originally present in the green ultramarine remains combined with a smaller quantity of sodium. The roasting is generally effected in an iron cylinder, somewhat similar to a gas-retort, sulphur being added until the required depth of blue is obtained. The ultramarine is then pulverised, lixiviated, dried, and assorted as to quality.

β. Soda-ultramarine is prepared from the following proportions of materials:—

Kaolin		 	100	100
Sulphate of soda		 	property (CO)	
Soda		 	90	100
Carbon		 	6	12
Sulphur	. :	 • •	100	бо
Resin		 	6	-

The ignition is effected in the manner previously described. By increasing the proportion of soda and of sulphur, blue ultramarine may be formed at one operation.

γ. Silica-ultramarine is prepared in a similar manner, silica being added to the former materials to the amount of 5 to 10 per cent of the kaolin. Blue

ultramarine is the immediate product of the calcination. The process, however, is difficult to manage, on account of the tendency to fusion amongst the materials employed.

CYANOGEN COLOURS.

The colouring materials of this group are-

Prussian blue;

Soluble Prussian blue;

Turnbull's blue (two varieties);

Tin blue (two varieties); and

Havraneck's green, or prussiate of chromium.

All these preparations are obtained by means of the yellow and red prussiates, or, as they are scientifically called, ferro- and ferri-cyanide of potassium. Prussian blue or Berlin blue was quite accidentally discovered in the year 1710, by Diesbach, at Berlin, whence its name. It was only towards the end of last century that Scheele discovered the relation existing between Berlin blue (ferrocyanide of cyanide of iron) and the yellow prussiate. This salt is technically a very important substance. It contains in 100 parts— Potassium, 37:03; cyanogen (carbon, 17:04; nitrogen, 19:89); iron, 13:25; water, 12'79. It is considered either as a combination of ferro-cyanogen with potassium and water (Fe₃Cy = Cfy)₂K + ₃HO; or as a combination of protocyanide of iron (FeC₂N=FeCy) with cyanide of potassium and water, FeCy+2KCy+3HO. The salt crystallises in large, deep, lemon-coloured crystals. It loses its water of crystallisation at 100°; dissolves in four times its weight of cold, and in a little more than its own weight of boiling water; insoluble in strong alcohol, which precipitates its aqueous solution. The specific gravity of its concentrated solution at 8° C. is 1.130; the specific gravity of the salt is 1.833. Heated to a dull red heat, with exclusion of air, and having been deprived of its water, the salt fuses, is decomposed, gives off nitrogen, and leaves a residue of cyanide of potassium and carbide of iron; but if any water has been left, and oxygen has access during this ignition, carbonic acid and ammonia are simultaneously given off. A mixture of 8 parts of dried ferrocyanide and 3 parts of carbonate of potash yields, on fusion, cyanide of potassium, carbonic acid and carbonic oxide, and peroxide of iron. The yellow prussiate and its aqueous solution are slowly decomposed by the action of daylight, hydrocyanic acid is given off, and there is formed either Prussian blue or oxide of iron; the solution assumes an alkaline reaction. The yellow prussiate is manufactured on the large scale: the rationale of the process is that as soon as nitrogenous substances, preferably of animal origin,-horn, blood, refuse wool, leather, and similar materials,—are ignited with potash (carbonate or any other salt of potash decomposable by heat and carbon), and some iron filings or borings, there are produced, by a complicate reaction, potassium and sulphide of potassium; the sulphur of the latter is transferred to the iron, and, by the intervention of the potassium and carbon, cyanogen is formed, which in its turn combines with the potassium. It should be borne in mind that cyanide of potassium resists, i. e. is not decomposed by, very intense heat. After cooling there does not exist in the fused mass ferrocyanide ready formed, but only cyanide of potassium and iron, and of course carbonaceous matter; the ferrocyanide of potassium is obtained by lixiviating the fused mass with water. The so-called red prussiate consists, in 100 parts, of

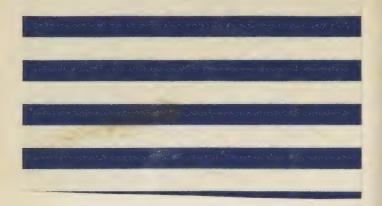
potassium, 35.58; cyanogen (carbon, 21.63; nitrogen, 25.54); iron, 17.29. This substance is considered to be either a combination of ferricyanogen ($2Fe+6C_2N=2Cfy$) and potassium, 2Cfy,3K, or as a combination of cyanide of iron ($2Fe,3C_2N=Fe_2Cy_3$) with cyanide of potassium, Fe_2Cy_3+KCy . It is prepared by submitting the yellow prussiate, either in the state of dry powder or in solution in water (the former is preferred), to the action of chlorine gas. As soon as the latter ceases to be absorbed the operation is finished. The saline mass is then dissolved in the smallest possible quantity of water, and the red prussiate crystallises out, chloride of potassium being left:—

2(2KCy+FeCy) + Cl = ClK + (Fe₂Cy₃+3KCy). Yellow Prussiate. Chlorine. Chloride of Potassium.

This salt, which forms beautifully ruby-coloured crystals, its powder being orange-coloured, is soluble in twice its weight of cold, and about its own weight of warm water; it is insoluble in absolute alcohol, and only very slightly soluble in weaker spirits. The crystals decrepitate on being heated, and yield, on being ignited in closed vessels, cyanogen and a little nitrogen; while the residue consists of cyanide of potassium, ferrocyanide of potassium, paracyanogen, and carbide of iron. This salt is an energetic oxidising agent, especially in the presence of alkalies; it converts, for instance, the protoxides of lead and manganese into peroxides; destroys indigo, converting it into isatine, on which account it is sometimes used as a discharge (Mercer's process).* Red prussiate is used by dyers for obtaining peculiar shades of blue. If cotton cloth be passed in the usual way through nitrate of iron, and rinsed, it will make no blue when put into red prussiate; but if it is afterwards passed into muriate of tin liquor, it strikes a blue directly, which has a good shade. Red prussiate is not much used in printing. It is found in some recipes for dark steam blues, and for a few other colours, such as myrtle and

As regards the colours known as Prussian blue we have to distinguish-(1). Neutral Berlin, or Prussian blue, which is obtained when a solution of the ferrocyanide of potassium is poured into any solution of a salt of peroxide of iron, preferably the perchloride; a very bulky deep blue precipitate is formed, which it is very difficult to free from the ferrocyanide by washing, and tenaciously retains a portion of that salt. (2). The basic Berlin blue is obtained when a solution of a proto-salt of iron is precipitated by means of a solution of the ferrocyanide; the precipitate is at first white, but gradually oxidation takes place, which may also be induced by oxidising agents, and the result is the formation of a blue substance, stated to be soluble in water; this solubility, however, is due to the presence of ferrocyanide of potassium. The Berlin blue of commerce is always a mixture of basic and neutral blue, or, in chemical terms, a ferrocyanide of iron; but the material as met with in the trade contains variable quantities of inert mineral matter, added for the purpose of diluting the colour, or for giving weight, and also as dryers. The substances so employed are chalk, pipe-clay, and the sulphates of lime and baryta. According to M. Pohl, there is met with in the trade a kind of Berlin blue that is adulterated with starch coloured blue by means of iodine.

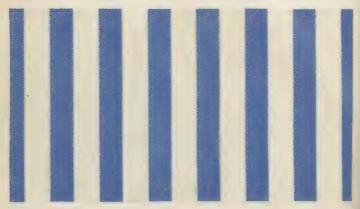
^{*} Although theoretically an excellent plan, it is not much used in practice, for two reasons, - one of these being its too quick action and the difficulty of properly thickening, and the other its expense.



DARK BLUE.

We subjoin specimens of printed cloth, light and dark blue styles, prepared by Messrs. Wood and Wright, Clayton Vale Print Works, Manchester. The dark blue is obtained by printing on the following compound:—

- 4 gallons of water;
- 8 lbs. starch;
- 3 lbs. sal-ammoniac;
- 9 lbs. yellow prussiate of potash;
- I lb. red
 - i ib. ied ,, ,,
- 6 lbs. tartaric acid;
- 3 lbs. persulphate potash;
- } lb. oxalic acid;
- 2 gallons prussiate tin pulp.



LIGHT BLUE.

The tin pulp is prepared from a mixture of the two following solutions, well stirred, and filtered to a pulp:—

a, I gallon of hot water;

r lb. of yellow prussiate of potash.

b. I gallon of water;

r lb. muriate of tin crystals.

The cloth when printed is steamed for 40 minutes, aged during one night, and rinsed in a weak solution of bichrome and alum at 120° F. It is then washed, dried, and finished, when it presents the appearance of the specimen.

The light steam blue is printed from the following standard mixture:-

45 lbs. prussiate of potash;

30 lbs. alum;

20 gallons of boiling water;

10 gallons of cold water;

3 pints of vitriol.

I quart of this standard is added to 3 quarts of water; there is then added—
1½ lbs. of starch; the bath is boiled, cooled, strained, and then is ready.

When printed the cloth is steamed for 40 minutes, then aged during one night, and rinsed in a weak solution of bichromate of potash and alum on the mangle. It is then passed through water, dried, and finished.

A beautiful Berlin or royal blue, almost approaching the aniline blues in lustre, is produced upon wool by the following process:—For 36 lbs. of wool, take yellow prussiate, 4 lbs., and oxalic acid, 6 lbs. Dissolve in water, and enter the wool at 100° F.; work well for 2 hours, raising the temperature gradually to 180° F. Take out and cool. Cool the liquor with 2 pailfuls of coldwater; add 21 lbs. alum; re-enter the wool, and work for ½ an hour. Then add ¾ pint of yellow spirit, and work for 1 hour, raising the temperature slowly to 180° F., at which heat work for 1½ hours longer. Take out and add 1 to 2 pints of nitrate of iron, according to shade required. Re-enter the wool, and give five or six turns. Take out, cool, and wash very well.

The yellow spirit referred to may be made as follows:—Take 18 ozs. tin crystals, 4½ lbs. hydrochloric acid, 2 lbs. strongest sulphuric acid, and 2 lbs. water. Dissolve the tin salt in the hydrochloric acid; mix in a separate vessel the sulphuric acid and water, and when cool mix altogether. Let down with water to 60° Tw.

Turnbull's blue is obtained by the action of ferricyanide of potassium (red prussiate) upon solutions of proto-salts of iron. These colours, as such, are not used in printing and dyeing. Alkalies destroy them. They are insoluble in water; and their so-called solution, used as blue ink, is merely the finely-divided solid matter in a state of suspension. These colours are fixed upon textile materials chiefly by two reactions. The goods are mordanted with a solution of iron,—in other words, the hydrated oxide of iron is deposited in the pores of the fibre,—and are then passed through a bath consisting of acidulated prussiate of potash. Or ferro- or ferri-cyanhydric acid, or a mixture of both, is applied to the tissues by passing them through an aqueous solution of the potassium salts mixed with an acid, and the blue colour is brought out by the simultaneous action of steam and the oxygen of the air. The addition of preparations of tin in these processes is not required for developing the colour, but only for modifying its shade. For dyeing wool a so-called royal

blue, the second method is exclusively employed. It appears that wool has a great affinity for Prussian blue when that compound is set free by heat from a solution of ferro-cyanhydric acid. The wool is therefore placed in a bath of a solution of prussiate mixed with a suitable quantity of royal blue spirits—a mixture of sulphuric, hydrochloric, and nitric acids. If the red prussiate be used the nitric acid is omitted as needless. The so-called prussiate of tin, or tin-pulp, is chiefly used as an ingredient in printing steam-blues on cottom. It is formed by mixing protochloride of tin and yellow prussiate. The latter should be separately dissolved in one half the water, the tin salt mixed with the other half, when both are poured together and allowed to settle. The following formulæ for preparing tin-pulp for steam-blues are in actual use, and will give an insight into its composition:—

Ordinary White Tin-Pulp.

	No. I.	No. 2.	No. 3.
Yellow prussiate of potash*	4 lbs.	8 lbs.	9 lbs.
Muriate (protochloride) of tin at 120° Baumé	2 qts.	5 qts.	б qts.
Water	6 gals.	10 gals.	10 gals.
Yield of pulp	2 gals.	4 gals.	6 gals.

The prussiate is first dissolved in one half of the water, the muriate of tin then mixed with the remainder of the water; the two solutions are then mixed together and well stirred, to break up the precipitate into a fine pulp, they are thrown upon a filter, or washed by decantation, and then drained down to the given bulk.

Blue Tin-Pulp.

Nine lbs. of prussiate of potash, 5 gallons hot water, 3 quarts of solution of bichloride of tin at 100° B., 5 gallons of cold water. The two solutions are mixed, well stirred up with about 12 gallons of water, and then drained down to 6 gallons. In mixing dark steam-blues it frequently happens that large quantities of hydrocyanic acid are developed from the hot colours, and sometimes men working over the pans or mugs are stupefied or sickened by the smell. There should therefore always be good and efficient ventilation; but in any serious case the sprinkling of liquid ammonia, and the inspiring of ammonia and alcohol mixed, as well as the immediate removal of the men affected into the open air, should be resorted to.

Among the methods in use for the production of Prussian blue by printing is the following:—The tissue is first passed through a bath of stannate of soda, next into a bath of very dilute sulphuric acid rinsed well in water and dried, and there is then printed on it a mixture of yellow and red prussiate of potash, prussiate of tin, tartaric and oxalic acids, and sal-ammoniac. The tissue is steamed and afterwards washed. Silk is dyed with Prussian blue by mordanting with a warm mixture of nitrosulphate of iron and bitartrate of potash, or, instead of the latter, protochloride of tin. The tissue or yarn is rinsed in water, and dyed by means of being passed through a solution of yellow prussiate slightly acidified with hydrochloric or sulphuric acid. Cotton is dyed blue also by this last method.

We retain here the names by which in actual practice these chemicals are known, although these names are not the most scientific.

French blue is obtained by the following process:—The tissue is treated twice with a solution of stannate of soda at 3°B.; then passed twice through a 1bath, composed of 12 parts of a solution of nitrate of peroxide of iron at 455°B., 1 part of tin-salt (crystallised protochloride), and 1½ parts of sulphuric accid. After rinsing through water the tissue is immersed in a bath, composed of 2 parts of yellow prussiate and 1 part of sulphuric acid and sufficient wrater.

Havraneck green is composed as follows:—I part of red prussiate, 4 parts of yellow prussiate, 2 parts of chrome alum, 9 parts of prussiate of tin in pulp, I part of tartaric acid, 24 parts of water thickened with starch. The colour is developed by steaming.

Cobalt Blues.

The substance known as cæruleum is a stannate of cobalt mixed with some suilphate of lime, the latter being unessential. The formula of this compound is $3(SnO_2,CoO) + SnO_2$. The pigment is not affected by atmospheric influence, lig;ht, or heat; it is neither affected by caustic alkalies or acetic acid, but is dissolved by mineral acids. It is blue also in artificial light. A factitious cæruleum is obtained by mixing ultramarine with Naples yellow and whitelead. Neither this cæruleum nor smalt (a cobalto-silicate), now only used for porcelain staining, nor Thenard blue (oxide of cobalt and alumina, or phosphiate of alumina with oxide of cobalt), a very beautiful blue, are now used as pigment colours for calico-printing.

None of the blue-coloured compounds of molybdenum and tungsten are at present used, either as dyes or as pigment colours, but the introduction of these colours may be expected within a few years.

CHAPTER III.

COLOURING MATTERS OF ORGANIC ORIGIN ARTIFICIALLY OBTAINED.

THE discoveries of scientific chemists made during the last thirty years have brought about the use, on a large scale, of substances suitable for dyes obtained by purely chemical reactions; in practice on the large scale there have been, however, a few instances of a somewhat similar nature, in so far as regards the obtaining of dyes and pigments from perfectly colourless materials. We may mention, as an example, the conversion of lichens under the joint action of air and putrid urine into a beautiful reddish violet matter long before scientific chemists proved that the colourable acids of these plants are changed first into orcine and then into coloured orceine under the influence of oxygen and ammonia. Among the colouring matters of organic origin artificially obtained, we distinguish the following groups:—(1). Colours derived from uric acid; (2). Colours derived from aniline and the oily non-oxygenated alkalies homologous, isologous, and analogous to aniline; (3). Colours obtained from phenol and substances analogous therewith; (4). Naphthaline colours; (5). Colours derived from vegetable alkaloids; (6). Some colouring matters of various origin. All these substances agree in this point, that carbon is an essential element of their constitution. Some of them contain beside, hydrogen and oxygen; others, again, nitrogen, in addition to the hydrogen, while the oxygen may or may not be present. As a consequence of their constitution these substances are unstable under the influence of high temperatures, and combustible, i.e., converted into water, carbonic acid, and nitrogen at a red heat with access of air; some of these substances are weak acids, others, again, strong alkalies comparable with ammonia, and not a few are quite neutral.

Colours Derived from Uric Acid—Purpurates, Murexide.

Purpuric acid, the ammoniacal salt of which is termed murexide, is one of the most interesting groups of a series of products of decomposition.* Murexide was discovered by Scheele in the year 1776, as a product of the splitting up of uric acid, $C_{10}H_4N_4O_6$, a substance which has not been hitherto artificially prepared. This material, when acted upon by nitric acid or other oxidising agents, is converted into urea, $C_2H_4N_2O_4$, a neutral substance, and into alloxan—

$$\underbrace{\left(\text{C}_{\text{10}}\text{H}_{4}\text{N}_{4}\text{O}_{6}\right)}_{\text{Uric acid.}} + \left(\text{NO}_{5}, \text{HO}\right) = \underbrace{\text{C}_{2}\text{H}_{4}\text{N}_{2}\text{O}}_{\text{2}} + \underbrace{\text{C}_{8}\text{H}_{4}\text{N}_{2}\text{O}}_{\text{10}} + \text{NO}_{3}.$$

^{*} It is better to apply here the term splitting up (Spaltung), as the Germans call it.

Since nitrous acid is simultaneously set free, the urea is immediately destroyed and converted into carbonic acid, water, and nitrogen—

$$C_2H_4N_2O_2 + 2NO_3 = 2CO_2 + 4HO + 4N,$$
Urea.

so that the result of the reaction of nitric acid is the formation of alloxan, a substance capable of crystallisation, soluble in water, of an unpleasant odour, and staining the skin red. Alloxan is one of those substances the molecules of which are en mouvement perpetuel, and, hence, prone to ready conversion into another substance called alloxantin, containing r atom less of oxygen—

This conversion of the former into the latter substance is effected by the action of reducing agents; for instance, nascent hydrogen, and also when alloxan is simply boiled with water. In the latter case parabanic acid is also formed, and carbonic acid given off; when a small quantity of an acid is added to the water wherein the alloxan is boiled alloxantin is also generated, but urea, oxalic, and carbonic acids are simultaneously formed. Alloxantin, accompanied by some alloxan, is directly formed when uric acid is treated with dilute nitric acid; from alloxantin, when treated with chloride of ammonium, is formed dialuramide, and from that substance murexide, or purpurate of ammonium (NH₄O,C₁₆H₄N₅O₁₁+2HO) is generated under the following circumstances:—(a) By the oxidation of dialuramide by means of the oxides of mercury or silver; (b) By the action of ammonia upon alloxantin; (c) By the action of ammonia or of carbonate of ammonia upon alloxan, or better, a mixture of alloxan and alloxantin; (d) By destructive distillation of alloxan by itself, or of that substance mixed with an organic body. For the manufacture of murexide on the large scale guano is chiefly employed as the source of uric acid, and the process adopted may be described in the following terms: - Peruvian guano* of best quality is placed in a suitable leaden vessel, and mixed with hydrochloric acid at 18° Tw., boiled therewith for one hour, while the mixture is kept well stirred up. The mass is next filtered through coarse linen and washed with water; the acid removes from the guano a quantity of inert salts, decomposing the combination of the uric acid and ammonia, setting the former free, since that substance in its free state is very sparingly soluble in water, and especially so when it contains an acid. The uric acid remains on the filter among the sand and other nondescript substances insoluble in hydrochloric acid of the above strength; the pasty mass left upon the filter is placed in a large porcelain dish, and mixed with its own weight of HCl at 40° Tw., and heated to 40°; when the action of the acid has been continued for a short time there is added to the mass the that part of the weight of the substance as when taken from the filter, of nitric acid, and the temperature kept steadily between 44° and 62°. This proceeding has the effect of converting the uric acid contained in the guano into alloxantine and alloxan; after a while an equal bulk of water is added to the fluid in the basin, and the whole left quietly standing to deposit insoluble matters, the

^{*} This guano contains a pretty large quantity of urate of ammonia, in addition to a host of other substances.

clear liquid is decanted, and the insoluble residue frequently washed with water; the clear solution thus obtained contains as its main constituent alloxan and alloxantin; the former of these substances is entirely converted into alloxantin by means of the reducing action of protochloride of tin, and precipitated in the shape of alloxantin; this precipitate having settled down the clear supernatant liquid is withdrawn, and the pasty mass thrown on a linen filter and washed with acidulated water. After having been carefully dried and reduced to powder, it is placed in a porcelain basin, set in another basin containing liquid ammonia, and put aside in a warm place until the powder has been entirely converted into a brilliant purple mass. In other words, it has been converted into murexide; since alloxantin forms, when it is in an atmosphere containing ammonia and water, murexide (purpurate of ammonia*).

Pure murexide when dry is a brilliant crystalline powder of metallic lustre and a golden greenish hue akin to that of the wings of Spanish flies. Placed between the eye and the light these crystals appear red, and when pulverised the powder is red. At 100° the crystals lose 1 molecule of water. Murexide is insoluble in alcohol and ether; sparingly soluble in cold water, to which it imparts a reddish hue; in hot water the solubility is greater. Murexide is far more soluble in solution of nitrate of lead, wherewith it does not undergo double decomposition. The purpurates of baryta, silver, mercury, and lead (if acetate be used) are insoluble in water. Murexide dissolves in an aqueous solution of caustic potassa, yielding a most magnificently blue solution, which becomes colourless on the application of heat. Murexide is now no longer used for dyeing or calico printing, having been superseded by the It was met with in trade in three different conditions, aniline colours. viz., as paste, as powder, and in crystals. The manufacture of this article required great skill and nicety of management, and, consequently, the substance was always expensive. Murexide was applied as a dye to silk and wool by mixing with corrosive sublimate, acetate of soda, and acetic acid. For printing, a mixture of murexide with nitrate of lead or acetate of zinc properly thickened is applied on cotton fabrics, which are then allowed to dry for a day or two, when the colour is fixed by passing them through a mixture of corrosive sublimate, acetate of soda, and acetic acid. A modification of this process was used very successfully some years ago by mixing a thickened solution of murexide in nitrate of lead, with a thickened solution of bichloride of mercury (these solutions do not precipitate each other for some twentyfour hours, and then only imperfectly). This colour was then printed on the cloth and aged two or three days, and fixed by simply running through a solution of acetate of soda. This allowed murexide colours to be printed along with, and after, other colours which would have been spoiled by running through a solution of bichloride or pernitrate of mercury, which latter salt was chiefly employed. Murexide on woven tissues can be detected-

r. By its beautiful and brilliant rose or purplish rose amaranth, which behaves with reagents in the following manner:—(a). The colour is destroyed by dilute mineral acids (hydrochloric, nitric, and sulphuric); (b). Caustic alkalies also destroy the colour, which, however, turns first blue; washing

^{*} Purpuric acid is not known in isolated state.

with soap gradually destroys the colour; (c). Reducing agents, as sulphurous acid, protochloride of tin, hydrosulphuret of ammonium, and protosulphate of iron, also rapidly destroy this colour.

Purple of the Ancients.

The use of a purple colour extracted from certain univalve molluscs dates back to a very remote period of antiquity. The tissues, chiefly linen and wool thus dyed, were always held in high esteem, and were extremely costly. The real art of applying this dye, and the precise kind of mollusc, are to a great extent matters of conjecture. Dr. Sacc has published a lengthy, yet very interesting, paper on this subject.* It is a positive fact that in different parts of the seas of our globe in hot, temperate, and even cold climates molluscs are found which contain in a peculiar organ a very thick yellowish green liquid, which gradually imparts to tissues a purplish colour. A Mr. William Cole, of Bristol, obtained a high reputation by the fact that he discovered, in the year 1663, the mollusc which had been for some time used by a dyer of that city to impart to tissues a brilliant and fast purple colour. Messrs. B. de Jussieu, Réaumur, Duhamel, and Bancroft experimented in the course of the last and beginning of this century with various molluscs for the purpose of dyeing tissues.

M. Gonfreville records that in some parts of India a mollusc, known as a murex, is kept alive in sea-water until a sufficient number is obtained; from 4000 to 5000 of these shell fish are required to dye r kilo. of wool, for which purpose the shells and contents are broken up while placed in sea-water, and left standing for several days afterwards in leaden vessels. The wool to be dyed is immersed in the liquid, or sometimes the liquid is applied to the tissue by means of a brush. According to M. de Saulcy, the ancients derived their purple from the Purpura hemastoma, known to Pliny as Buccinum, and also from the Murex brandaris, which Pliny called Purpura. At Athens and Pompeii large quantities of these shells have been discovered lying in heaps close to ancient dye-works. The ancients distinguished Tyrian and Byzantium purple; the former had the colour of coagulated blood; the latter exhibited a more violet hue. Both were in every respect fast colours.

Colours Derived from Aniline and Kindred Bodies.

Aniline was first discovered in 1826 by Unverdorben among the products of the destructive distillation of indigo. Runge extracted from coal-tar a substance which he named Kyanol, which, when treated with hypochlorite of lime, yielded a brilliant blue colour, and which was afterwards proved to be identical with aniline. Up to 1856 this substance remained a mere laboratory curiosity, devoid of industrial application. To Runge the honour is, therefore, due of having first drawn attention to the possibility of obtaining aniline from coal-tar, and of applying it to the production of tinctorial substances. Fritzsche found that aniline yields with aqueous solution of chromic acid a bluish-black precipitate. In 1853, Beissenhirtz described the blue colour resulting from a mixture of aniline, bichromate of potassa, and sulphuric acid. Stenhouse, when experimenting on furfurol, found that aniline and its acetate

^{*} Bulletin de la Societé de Mulhouse, vol. xxvi., p. 305.

yield with the former substance a magnificent carmine-red colour. Natanson, in 1856, showed that when aniline and chloride of ethyl (Dutch liquid) are heated together in sealed tubes to 200°, the mixture assumes a beautiful blood-red colour. Professor Hofmann discovered a product resulting from the action of tetrachloride of carbon upon aniline, which yields a brilliant carmine colour soluble in alcohol. It is, however, quite impossible to give, in our allotted space, a historical review of the numerous discoveries made in this immense field. The most distinguished investigators in this department are Messrs. Perkin, Verguins, Mansfield, Collas, Zinin, Gerber-Keller, Heilmann, Medlock, Nicholson, Girard and De Laire, Hofmann, Lightfoot, &c.

We will now proceed to examine, first, the primitive material aniline, and the sources whence it is obtained, and, secondly, the coloured derivatives

which it is capable of yielding.

Aniline (kyanol, of Runge; crystalline, of Unverdorben; nitride of phenyl and hydrogen; phenylamine; benzidam) has the composition $C_{12}H_7N$. It contains, in 100 parts—C, 77'41; H, 7'54; N, 15'05. When pure it is a colourless, highly-refractive liquid, of the sp. gr. 1'028 at 15° C. Its vapourdensity is 3'220. It boils at 182° C., and does not congeal at -20° C. It is volatile at the ordinary temperature of the atmosphere. It has a faintly aromatic unpleasant odour, and an acrid, burning taste. It is slightly soluble in water, from which it may precipitated by common salt. With alcohol, ether, aldehyd, and the fixed and volatile oils it can be mixed in every proportion.

Aniline combines directly with the hydracids and the hydrated oxacids, forming salts similar to those of ammonia. These compounds are nearly all soluble in water and alcohol, and are capable of assuming the crystalline form. The alkalies and alkaline earths displace aniline from its combinations with acids, but aniline decomposes the salts of iron, zinc, and aluminium, precipitating the hydrated oxides of those metals. In contact with air aniline rapidly alters its colour, becoming brown, and is finally converted into a resinous mass. Its salts, when pure, are colourless, but in contact with the air they gradually assume a reddish colour. Solutions of the aniline salts colour firwood and elder-pith a deep yellow, which is not discharged by chlorine. This colour is apparent when only 1-500,000ths of aniline is present.

Aniline and its salts may be detected by the following reactions:—When a small quantity of any aniline salt is placed upon a plate of white porcelain, and mixed with a few drops of concentrated sulphuric acid, and a few drops of a solution of chromate of potassa are next added, a beautiful blue colour is formed, which very soon disappears. A solution of an alkaline hypochlorite, when mixed with aniline or any of its salts, gives rise to a violet-blue colour, also fugitive. If a single drop of a solution of I part aniline in 1000 parts dilute sulphuric acid (I part monohydrated acid in 7 of water) is placed on a piece of platinum-foil, and brought into contact with the positive pole of a single Bunsen galvanic cell, an intense blue colouration is instantly produced, which passes successively to violet and rose-red when the drop is touched with the negative pole.

Perfectly pure aniline may be obtained by distilling indigo and isatine with the hydrates of potash and soda. Anthranilic acid, a product of a hot, concentrated solution of potassa upon indigo, is decomposed into aniline and carbonic acid by distillation with caustic lime. It is scarcely needful to

remark that the aniline of commerce is not prepared in this manner. Its source is coal-tar, which contains, according to the most recent investigations, upwards of fifty distinct bodies. These are classified in three groups, according as they are acid, neutral, or basic. Others divide them into hydrocarbons, consisting of hydrogen and carbon only; oxygenated or sulphuretted compounds free from nitrogen; and, lastly, nitrogenised compounds, analogous to ammonia. Amongst these aniline also occurs, but in so small a proportion, scarcely amounting to 0.5 per cent, that it is of no practical value. It may, if desired, be extracted by treating the products coming over between 150° and 200° C. with dilute sulphuric acid, and subsequent decomposition of the sulphare of aniline thus obtained with hydrate of soda or milk of lime. Hofmann's process, described in the Annalen der Chemie und Pharmacie, vol. xlvii., p. 30, may be also applied. Aniline is therefore manufactured in an indirect manner from benzine or benzol,—another of the coal-tar products, which thus becomes the starting-point of the aniline colours.

Benzol was discovered by Faraday, early in the present century, among the products of the oil gas manufacture. It is obtained pure by distilling benzoic acid with three times its weight of hydrate of lime. By this process benzol is obtained as a colourless, highly mobile fluid, of sp. gr. o.85, and boiling at 85° C. When cooled down to o' C., it forms a crystalline mass, which liquefies at 7° C. Benzol is insoluble in water, but dissolves readily in alcohol and ether. It is a true hydrocarbon, consisting only of carbon and hydrogen. Its formula is C12H6. This substance is present in the state of vapour in common coal-gas, from which it may be extracted by treating the gas at a low temperature with alcohol, or, better, petroleum oil, from which solvents the benzol is separated by rectification at a very gentle heat. As yet benzol is chiefly, if not solely, obtained from coal-tar. This liquid is distilled in suitable apparatus.* The benzols (mixtures of hydrocarbons homologous with true benzol), which pass over between 80° and 100° C. are called light benzols. Those collected from 100° C. to 130° C. are known as heavy benzols. The products thus obtained are converted separately into nitro-benzols. The benzols of commerce consist chiefly of the hydrocarbons, benzol, and toluol, cymol and cumol being present in small quantities only.

To give an idea of the contents of several species of coal-tar, we add here the results of investigations made on this subject by Dr. Crace Calvert.

				Benzois.	Phenic acid.	Heavy Hydrocarb,	Paraffin.	Naphthalin.	Dry tar.	
The tar of	Boghead coal	cont	ains	 I2	3	30	4 I	O	14 P	.c.
7.1	Cannel			 9	14	40	0	15	22	11
,,	Newcastle			 2	5	12	0	58	23	2.2
,,	Staffordshire			 5	9	35	0	22	29	9 9

The benzol is treated with a mixture of strong nitric and sulphuric acids, and is thus converted into nitro-benzol, $C_{12}H_5NO_4$. This latter substance is converted into aniline by means of a process invented by Bechamps. 100

^{*} See Reimann's Handbook of Aniline, p. 3.

	Shades of the Colours on Stuffs.	Dirty violet Slate-blue. Much	Red violet j viol-aniline.	Red violet (Mauvaniline mixed with a little red.	Red.	Red.	Red.	Red.	Red. Containing much	red. chrysotoluidine.	Red.	Red.
	Colour obtained as compared with crystal magenta=1000.	'n	20	IIO	160	230	270	240	260	260	200	180
	Sp. gr. of the anilines at 16 C.	I.0205	1.0199	1810.1	1.0139	6010.1	0900.I	8100.1	6000.I	0.0975	0.6643	0.6656
TABLE A.	Boiling-points of the anilines.	180°185°	180°-185°	185°—190°	185,-190°	190°—195°	195°-200°	195°-200°	200°205°	200°-205°	205°-210°	205°-210°
TAI	Amount of aniline yielded by 100 parts of the nitro-benzin.	59	55	56	63	99	73	74	69	74	73	74
	Sp. gr. of the nitro benzols at 16° C.	1651.1	2191.1	1.1577	1.1445	1.1425	1.1365	6181.1	1.1235	1.1187	1.1182	1.1093
	Boiling-points of the nitro- benzols.	205°-210°	205°-210°	210°-215°	210°-215°	215°-220°	220°-225°	220°-225°	225°230°	225°-230°	23.0°	23.0°235°
	Sp. gr. of the benzols at 15° C.	8116.0	0.9263	0.9154	9.9210	6806.0	1206.0	0.3048	0.6033	0.0022	6006.0	1006.0
	Benzols classed by their boiling-points.	83°-84°	80°-85°	85°-90°	90°- 95°	95°-100°	100°-105°	105°-110°	110°-115°	115°120°	120 -125	125,-130°
		a.	<i>b</i> .	ر٠	d.	•	۶.	مع	11.	• ••	٠٠,	k.

parts of nitro-benzol are mixed with an equal quantity of acetic acid and 200 parts of iron filings, when the following reaction ensues:—

8Fe+C₁₂H₅NO₄+8HO+12C₄H₃O₃=4(Fe₂O₃·3C₄H₃O₃)+C₁₂H₇N+6H. The mixture, after the addition of a quantity of lime sufficient to decompose any acetate of aniline which may have been formed, receives a current of steam, preferably superheated, which carries over the aniline, partly dissolved and partly in a state of mechanical suspension, into a condenser. When cold the aniline settles out of the water and is readily collected.

The products met with in the market under the name of aniline vary exceedingly. It may, indeed, almost be said that we meet with as many qualities as makers. The boiling-points vary from 180° or 182° to 195° C., and again from 200° to 210° C. The chemical characters vary according to the nature of the benzol employed. The following table illustrates these variations. Eleven kinds of benzol were taken, and their boiling-points and specific gravities having been noted, they were converted into nitro-benzols. Here, again, the boiling-points and specific gravities were observed, and they were transformed into anilines. The amount obtained, the specific gravity, and boiling-point of each was registered, and the anilines having been finally converted into magentas, the yield and quality was tabulated in each case.

Table B shows the nature and composition of some mixtures made with the above anilines, as well as the yield of these mixtures in colouring matter. These mixtures consist of equal parts of two or more of the anilines shown in Table A.

TABLE B.

Mixt Differ		of the		Boiling-points of the corresponding Hydrocarbons.	Relative Amounts of Colour obtained compared with Crystalline Rosaniline.	Shades on Stuffs.
b+c				80°— 90°	16	Very violet red. Rosaniline and mauvaniline.
d+e				90°—100°	17	Red.
f+g				100°110°	32	Red.
h+i				110°—120°	24	Reddish-yellow. Rosaniline and chrysotoluidine.
j+k				120°—130°	18	Red.
b+c+	d+	e		80°—100°	24	Red violet.
d + e +	$f+\xi$	·		90°—110°	37	Red.
f+g+	-h+	i		100°-150°	31	Red.
h+i+	j+k			110°—130°	19	Red.
b+c+ +h	d+i+i+i	e+f-j+k	+ g)	80°130°	25	Red.

To ascertain the commercial value of samples of aniline a careful determination of the boiling-point is always sufficient for the purposes of the manufacturer. The absence of water, benzol, and nitro-benzol, must first be proved. The presence of water and benzol is directly seen, upon submitting a portion to distillation, both by the thermometer and by examination of the first few drops which come over. Nitro-benzol is easily detected by saturating the suspected aniline with pure hydrochloric acid. If free from nitro-benzol the mixture will remain perfectly clear. Even a slight trace of nitro-benzol is sufficient to render the mixture milky.

Luxer ascertains the value of commercial anilines by estimating the amount of red colour which they respectively yield. Five grammes of the aniline in question and 5 grammes of syrupy arsenic acid, of sp. gr. 2'059, are heated to 150° for several hours, in the oil-bath, until the formation of a reddish-brown substance, with a greenish reflection, which on cooling becomes a hard, brittle mass. This is exhausted with boiling water, and made up to the bulk of I litre: 50 c.c. of this solution are taken and diluted with water to ½ litre, and in this fluid 6 grms. of woollen yarn are dyed, and the resulting samples compared as to intensity and tone. This test is considered fallacious by many practical men, as with such small quantities the regulation of the temperature is very difficult. Thus a variable quantity of aniline may remain unacted upon. It is necessary that the manufacturer should previously satisfy himself what boiling-points of aniline, or of a mixture of aniline and toluidine, are best adapted for his purpose. This having been done he will find the boiling-point a valuable guide.

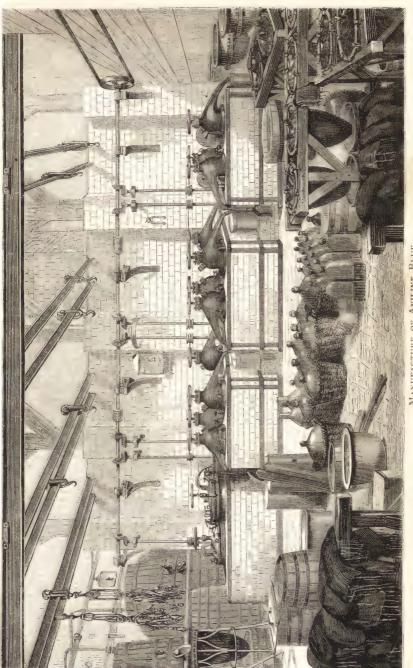
Reimann, to distinguish the so-called light from the heavy anilines,—or, as he names them, kuphaniline and baraniline,—heats slowly a certain quantity of any sort of aniline oil, and notes the quantity which distils over at various temperatures, degree by degree. More simply, the quantities are noted which distil over during a rise of 5 degrees. The quantities of distilled oil may be measured by receiving them in a graduated cylinder.

He puts 100 c.c. of kuphaniline in a glass retort, placed in an oil-bath heated by a lamp. The tube of the retort is joined to a Liebig's condenser, at the extremity of which a graduated cylinder is placed to receive and measure what distils over. The condenser is supplied with water in the usual manner; a thermometer is placed in the neck of the retort, and heat applied. Up to 180° C., 8½ c.c. passed over; from 180° to 185°, 54 c.c.; and from 185° to 190°, 34 c.c.; so that, say, 3½ remained in the retort. Other samples of light aniline yield numbers, not indeed identical, but similar.

Heavy anilines treated in the same manner allow only 3½ c.c. to pass over up to 190° C. From 190° to 195°, 8 c.c. distil over; up to 200° C., 18; to 205° C., 39; from 205° to 210°, 19; and from 210° to 215°, 7 c.c.; 5½ remaining in the retort. All the anilines of commerce are mixtures of light and heavy aniline in various proportions, and they distil over at intermediate temperatures, according to their composition. By distilling the following mixtures—

90	per	cent	kuphaniline	with	IO	per	cent	baranilin
85	5		22		15			21
80			9.9		20			9.9
75			29		25			2.7
62	_		99		37	ł		2.9
60			99		40			27
50			29		50			2.9
37	7 1		39		62	1		9.9
25	5		99		75			91

—and adding to the result the numbers given above, found by distilling pure kuphaniline and baraniline, he has constructed the following table, where K denotes light and B heavy aniline:—



MANUFACTURE OF ANILINE BLUE.



1)eg. C.	roo K o B	90 K 10 B	85 K 15 B	80 K 20 B	75 K 25 B	621 K 371 B	60 K 40 B	50 K 50 B	37½ K 62½ B	25 K 75 B	100 K 100 B
180°	21/2	7	$2\frac{1}{2}$	5 1/2	3 1/2	4		4	2	3	*****
*	6				3 1/2	3		3	2	$2\frac{1}{2}$	_
185°	54	50	291	22	$5\frac{1}{2}$	21/2	7	$4\frac{1}{2}$		21/2	
-metallia.			_		_		_	_			2
190°	34	34	561	55½	55½	41	37	71	5 1/2	$4\frac{1}{2}$	Ι½
195°		5	71/2	81	15	25	33	42	40	17	8
200°		_			9	81		19	281	36	18
205°	_			-	4 1/2	5	16	10	II	16	39
210°	_	_				4 ½		3 1	7 ½	8	19
215°								-		41/2	7
Residue	3 1/2	4	4	81	3 ½	61	7	61	3 4	5	54

All that is required is to distil over a sample in the manner described above, note the quantities coming over at different temperatures, and compare the tigures thus obtained with the table. In this manner the composition of a sample may be ascertained accurately enough for all practical purposes.

The aniline of commerce is a mixture of pure aniline and toluidine in variable proportions, the former preponderating in the light, and the latter in the heavy samples. Odorine and other substances are also present in small amount. Its colour is darker than that of pure aniline, and its smell more offensive.

Toluidine, C₇H₉N, was discovered by Muspratt and Hofmann ("Annalen der Chemie und Pharmacie," vol. liv., p. 1). It is a solid, crystalline body, which liquefies at 40° C. and boils at 198° C. It has an odour like that of aniline, and a burning taste. It is soluble in wood-spirit, alcohol, ether, aceton, and in the volatile and fatty oils. It forms with the acids a series of crystalline salts, most of which are soluble in water. Its acid solutions stain fir wood and elder pith a deep yellow, just like aniline. With hypochlorite of soda it yields, not a violet, but a reddish tinge. With nitric acid it becomes a deep red, whilst aniline gives an indigo-colour, and with chromic acid it furnishes a brown precipitate. The toluidine of commerce is obtained from nitro-toluol, in the same manner as aniline is obtained from nitro-benzol.

The methodical classification of the coloured reactions of aniline is not free from difficulty, as some of the results have not been scientifically investigated. The fact is that many manufacturers used in their experiments commercial anilines of unknown composition, and did not care to examine either the exact nature or origin of the tinctorial substances obtained. Under the common name of "aniline colours" we find included bodies which result from the simultaneous action of other bases. It should further be observed, that one and the same chemical reagent is capable of giving rise to several coloured derivatives, according to the time of action, temperature, degree of concentration, &c. Still we generally find a primary result of the reaction, the others being merely by-products, or, indeed, impurities which it is difficult to remove. We shall give such facts only as are of practical value, or which serve to clucidate the history of the aniline manufacture. The following colours are derived from aniline:—

ANILINE REDS.

Magenta, Fuchsine, Azaleine, Roseine, Rosaniline, Aniline Crimson, Rubine, and a variety of other trade names.

Aniline red, though not historically the first of its class, is scientifically and commercially the most important. In addition to its direct applications in dyeing and printing, it serves as the raw material for the manufacture of most other aniline colours. The production of this colour was first observed in 1856, by Natanson. Subsequently it was obtained by Hofmann, as a result of the reaction of tetrachloride of carbon upon aniline, and by Verguin, who substituted the anhydrous bichloride of tin for the carbon compound.

Hofmann's process is still in practical operation on the large scale at the establishment of Gerber-Keller, at Mulhouse. Three parts of aniline are treated together with one of chloride of carbon to the temperature of 170° to 180° C. (347° F.), of course under pressure. After several hours a brown-red mass is formed, which is treated with water, the extract evaporated to dryness, and the residue again extracted with alcohol, to take up the colour. ("Comptes Rendus de l'Academie des Sciences," vol. lxvii., p. 492). The red colour thus obtained is said by some to be quite distinct from common magenta, and is known in commerce as Hofmann's red. Reimann, however, is of opinion that the difference between this colour and magenta depends merely upon an unimportant admixture.

Renard Bros. and Verguin, of Lyons, patented the following process in 1859. They make use of small melting-pots of enamelled cast-iron, containing about 20 kilos. Into each of these they introduce 10 kilos. of aniline, and afterwards add by degrees 7 kilos. of anhydrous bichloride of tin, constantly stirring. The mixture is made under a hood communicating with a chimney, in order that the dense irritating vapours disengaged may be carried off as they are produced. As soon as the ingredients are incorporated, the pots are exposed to a naked fire in a small furnace, and raised to the boiling-point for 20 or 30 minutes. The mass remains fluid, and passes gradually from yellow to red, growing darker till it appears black. The product is tried from time to time, and as soon as it appears of an intense, bright, pure red, when spread in a thin layer upon a piece of white porcelain, the operation is stopped. The hot liquid matter is poured into stoneware jugs, and sold in this state without any purification.

This process of Gerber-Keller, Durand, and Schlumberger consists in heating in an oil-bath, in a suitable apparatus, up to the boiling-point, ro parts of aniline with 7 to 8 parts of nitrate of mercury, very dry and finely powdered. By degrees the mass becomes brown, and is transformed into a fine red liquid. The operation is then concluded, and the liquid is withdrawn from the fire, when it begins to thicken, puff up, and give off yellow vapours. It is then poured, in a thin stream, into two or three times its weight of boiling water, with constant stirring. The unconverted aniline floats on the surface, and the residue is taken up and treated again with boiling water as long as anything is dissolved. These liquids are precipitated with common salt, and the deposit collected on a filter. The following conditions must be observed:

—The operation lasts 8 to 9 hours, and the nitrate of mercury is added in very small portions at once, with constant stirring. The colour prepared in

this manner is sent into market without any purification, under the name "azaleine."

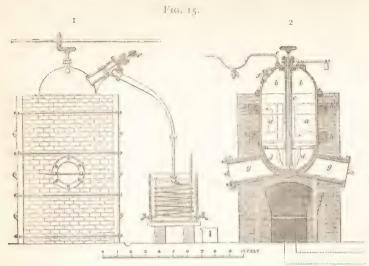
During the operation the mercuric nitrate is reduced to the metallic state. Allmost the whole of the mercury can be recovered, re-converted into nitrate off mercury, and used afresh in the preparation of azaleine. The bulk of the nitric acid can be recovered as an alkaline nitrate. Next to the arsenical method, this is the most economical procedure.

Lauth and Depouilly heat 6 to 8 parts of aniline to 150°—160° C., with I part nitrate of aniline. The fire must be removed as soon as the reaction becomes lively, or the mass will ignite. After the expiration of several hours a mass is obtained of a fine violet-red colour, which may be purified by booiling with 20 parts of water, when the unconverted aniline rises to the surface of the liquid as a scum, and is removed. The solution is then filtered through sand, and on cooling deposits a green paste with a metallic reflection. This process yields only 7 to 8 per cent of colouring matters, and the purification is difficult.

A variety of other oxidising agents have been proposed, such as phosphate and acetate of mercury, nitrate of lead, free nitric acid, aqua-regia, nitrate of anttimony, iodine, iodide of mercury,—in fact almost every metallic salt. The expense and inconvenience of most of these processes has caused them to be quitetly abandoned, and prevented an immense amount of litigation. A recent proposal deserves serious attention. Aniline is heated with nitro-benzol. The yield is asserted to be very large, the process simple, and the subsequent purification easy.

By far the largest part of the magenta of commerce is prepared by the arsenic acid process, which we shall therefore describe in some detail.

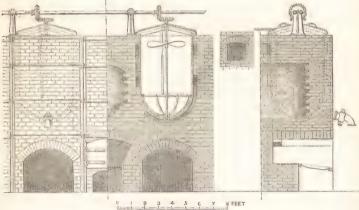
Al commercial aniline is selected, containing as nearly as possible 3 parts of anilline with I of toluidine, which is obtained by mixing 75 per cent of kupihaniline and 25 per cent of baraniline: 800 kilos, of this aniline and 1370 kiloss. of a solution containing 72 per cent of anhydrous arsenic acid are introduced into the apparatus (Fig. 15). The still, capable of holding 25000 litres, is fitted with a stirrer, worked by steam-power. A wide tube descends, parallel with the axis of the agitator, to the bottom of the appearatus, and serves to introduce steam. In the upper part are a man-hole, a saifety-valve, and a tap in communication with a tank of hot water. Below are ttwo large holes for emptying. The neck of the still communicates with a largee worm, which serves to condense the aniline volatilised in the course of the process. The temperature should not exceed 190° to 200° C. The operation lasts 8 to 10 hours. When the transformation is complete, about 850 litress of a mixture of aniline and water will have been condensed and collected, which, if separated by the addition of common salt, yield 440 kilos. of anilime and 420 of water. When 800 litres of the mixture have passed over, the ffire is withdrawn, as the apparatus will still retain heat enough for the termination of the process and for completing the volatilisation of the free anilime. During this time the agitator must be kept in constant motion. Stearm is now allowed to enter by the descending tube, and sweeps away mechanically the raw aniline yet remaining in the still. By degrees boiling water is now introduced, whilst heat is again applied to the apparatus. When the mass has become a homogeneous liquid, which is effected in about an



1. Elevation of complete apparatus. 2. Section.

Body of retort. b b. Head of retort. c. Axle of agitator, made hollow so as to conduct steam to the bottom of the apparatus. c. Entrance for steam. f. Manhole. g g. Openings for taking out the colour. h h. Cavities in which hot air circulates, and which can be opened if it is required to cool the apparatus.

F1G. 16.



hour, the vent-holes are opened, and the contents run into cisterns fitted with agitators through sheet-iron pipes (Fig. 16). Here the mass is treated with boiling water, in the proportion of 300 kilos, of crude magenta to 1500 litres of water, acidulated with 3 kilos, of hydrochloric acid. Ebullition is kept up by means of steam-pipes. In four or five hours the solution is complete.

The liquid is run, through large filters of woollen cloth, into large sheet-iron reeservoirs, holding 8 to 10 cubic metres each, and so arranged that their conteents can be heated by currents of steam. The filtrate, which no longer contains any matters insoluble in water, consists of solution of hydrochlorate, anrsenite, and arseniate of rosaniline, along with free arsenious and arsenic acids. It is now necessary to eliminate the arsenic. For this purpose, and foor every 200 kilos. of raw colour, 240 kilos. of common salt are added to the lidquid in small quantities at a time. The decomposition is accelerated by bblowing in steam, the final result being hydrochlorate of rosaniline, and, on the other hand, arsenite and arseniate of soda. The rosaniline compound, boeing insoluble in strong saline solutions, separates out and rises to the suurface. The liquid is cooled, the colour collected, and, after a few days, the mnother-liquor is run into large tanks, where it deposits the small amount of coolouring matter still held in suspension.

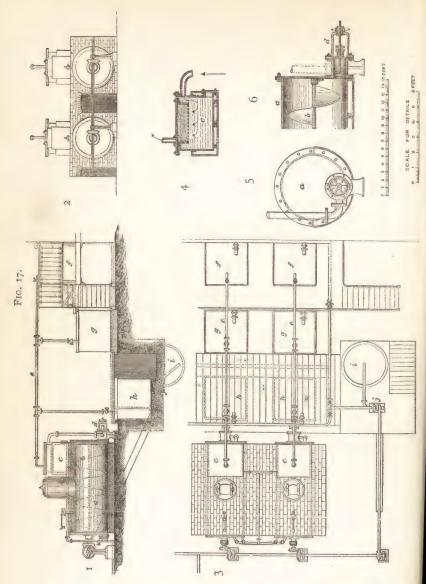
The colour thus obtained is washed with boiling water, in small quantities, too remove the chloride of sodium and the bulk of the arsenical salts which it t still retains.

If a higher degree of purity is required, it is re-dissolved in boiling water, fillitered, and allowed to crystallise.

There is a method of effecting the solution of the crude aniline red under processure. This procedure saves time and labour, lessens the quantity of water employed, giving consequently a more saturated solution, and abridging the filltrations. The apparatus is represented in Fig. 17.

The colour thus obtained is the hydrochlorate of rosaniline, a base having thae composition C₂₀H₁₀N₃,H₂O. This base, when uncombined, pure and cryystalline, appears in the form of small tables or needles, which if preserved froom the action of the air are colourless, but redden rapidly on exposure. It paasses from a colourless state to a rose, or even red condition, on fusion. without any change of composition. It is inodorous in the cold, but when hezated gives off a scent of diphenylamine. Its taste is rather bitter. Its speecific gravity is 1.8. It melts in boiling water, and is decomposed at 220° C. If kept for ten hours, or upwards, at the temperature of 210° to 220° C., it is graadually transformed into a violet colouring matter, insoluble in water, and butt sparingly soluble in acetic acid and boiling alcohol. Rosaniline dissolves in I boiling water to the extent of 2 or 3 grammes per litre, and is chiefly re depposited as the liquid cools. A litre of ammonia dissolves 4 grammes. In sodda and potash lyes it is soluble to about the same extent. Lime-water disssolves 3 grammes, and baryta-water rather more. In alcohol it dissolves to the extent of 10 grammes per litre. Wood-spirit, acetone, carbolic acid, andd aniline dissolve it freely; the latter in all proportions. On the other hannd, it is insoluble in ether, benzol and its homologues, and bisulphide of carbbon. It is soluble in almost all acids, mineral and organic, forming well defifined salts, which crystallise with great facility.

RRosaniline is a powerful base, displacing ammonia from its combinations with acids at 100° C. The coloured solutions of rosaniline and of its salts are: completely decolourised by caustic and carbonated alkalies, but the colour is reestored by the addition of a sufficient quantity of an organic acid. Proto chlooride of tin decolourises them at ordinary temperatures. Tree chlorine first changes the colour to blue, and then destroys it. Chloride of line rapidly



1, 2, 3. Elevation, profile, and ground plan of the entire apparatus.

4. Section of a filter.

5, 6. Elevation and section profile of one end of the extraction-boiler.

Boiler containing crude magenta melt and water, which are heated to about 130° C. (pressure about 2 atmospheres). b. Spiral agitator. c. Filter working upwards, under pressure from the boiler. d. Valve for opening or shutting communication between the boiler and the filter. e. Tube conducting the liquid at will into the vats, f, g, h. These are placed at different heights. In f a part of the colour is deposited; a further portion settles in g, and almost the whole remainder in the crystalliser, h, whence the liquid flows into the well, i, from which it is drawn up by the pump, j, for a new operation.

decolourises the salts of rosaniline. Permanganate of potash transforms the solutions of rosaniline and its salts into liquids which give merely a yellow dye. Rosaniline, whether free or in combination with acids, if dissolved and submitted to prolonged ebullition along with oxidising agents,—such as peroxide of lead, bichromate of potash, alkaline and alkaline earthy nitrites, and peroxide of barium,—is transformed into other colouring matters, brown or orange-red, according to circumstances.

The hydrochlorate of rosaniline, known as fuchsine, as obtained by the above process, although sufficiently pure for many operations in dyeing and

printing, requires for certain purposes further purification.

The simplest manner of preparing free rosaniline is to dissolve the hydrochlorate in boiling water, and to decompose it by means of a slight excess of an alkaline solution, also boiling. Ebullition is kept up for some hours; the liquid is filtered, and on cooling deposits magnificent crystals of rosaniline, almost colourless.

The acetate of rosaniline, known commercially as roseine, is the most important salt of this base. The rosaniline employed in its preparation should be pure and crystalline. It must be completely freed from the excess of alkali used in its preparation, dried, and pulverised. The acid should be entirely crystallisable, perfectly pure, and free especially from sulphuric and sulphurous acids. Calcareous waters should also be avoided. The rosaniline, fresh from the drying-stove, is placed in vessels of enamelled cast-iron, heated in the water-bath or by steam. Acetic acid is very gradually added, the mixture being carefully stirred till it becomes quite homogeneous. To promote combination the whole is heated to 60° or 70° C. Boiling water is then rapidly poured upon the semi-fluid mass, and it is kept in ebullition for some minutes. The liquid is run into crystallising vessels, set in a cool place not subject to variations of temperature, and after standing a few days deposits fine crystals of roseine. The best proportions are 20 parts of crystalline acetic acid to 100 parts of rosaniline. To dissolve these 120 parts of acetate of rosaniline, 240 to 250 parts of water are needed. The heat must be carefully managed. to avoid loss of acetic acid by volatilisation. Too prolonged boiling wastes the acid, and determines the formation of sub-salts which cannot be made to crystallise.

Roseine can also be formed by double decomposition, adding the solution of the crude arseniate, sulphate, &c., of rosaniline to a solution of acetate of lead. The method is unprofitable, as the precipitated lead forms a lake with a part of the colouring matter, which is thus practically lost.

Violaniline, mauvaniline, and chrysotoluidine are invariably present in small quantity in crude rosaniline as prepared by the arsenical method. These bases form collectively about one-half of the colouring matter contained in the crude product. When separated they furnish useful dyes. For the process of their isolation we must refer the reader to the work of Girard and De Laire, "Traité des Dérivés de la Houille," p. 575.

We must now turn to the practical application of magenta in dyeing and printing. It is abundantly used, not merely in rose, pink, and red shades, but in a variety of compound colours. Like most of the coal-tar colours, it has a strong affinity for animal tissues, upon which it produces solid shades without the aid of a mordant. Vegetable fibre, on the other hand, acquires merely

a fugitive stain, and requires, therefore, the intervention of a mordant. The first step is the solution of the colour. One of the best methods for woollens is to arrange a small flannel filter at one corner of the dye-beck, with its bag dipping below the surface of the liquid, but with its edges above. The requisite quantity of magenta crystals is weighed out, wrapped carefully up in a piece of clear flannel or close-grained calico, and allowed to dissolve in the hot water.

It is very important that no particles of undissolved magenta should be allowed to escape into the dye-bath, as they will attach themselves to the goods and form intense red or even bronzed spots. This precaution is particularly necessary in piece dyeing. As the affinity of magenta for woollen tissues is very great, without care the shades produced will be uneven. It is, therefore, well to dissolve only part of the requisite amount of magenta at once, wincing the pieces very rapidly in the weak-coloured liquid. The pieces or yarns are then lifted out of the dye-beck, the rest of the colour dissolved, the goods re-entered, and worked till the required shade is obtained.

For silk and cotton dyeing, where the dye-beck is not at so high a temperature, and where, consequently, the magenta cannot be readily dissolved in the manner above mentioned, the colour is previously dissolved and added to the dye-bath. When the aniline colours were first introduced the magenta crystals were dissolved in hot alcohol or methylated spirit, boiled for about a quarter of an hour, very carefully filtered through flannel, and preserved till wanted in stoppered bottles. In dyeing, the necessary amount of this solution was added to the dye-beck. This method was open to several disadvantages, as the cost of the alcohol, and its gradual evaporation during the process of dyeing, when the magenta was apt to separate out as a bronze scum, and to soil the tissues. Worst of all, the employment of a large quantity of alcohol was found to render the colours flat and dull. Great care is needed in the selection of a commercial alcohol for use along with magenta. It must be free from shellac-a common impurity. If this is present the colour works flatter and has a bluish tone, which is not desirable. Shellac may be easily detected by adding a little of the suspected spirit to an excess of water when the shellac is deposited. Pure alcohol when heated with r per cent of pure caustic potash should turn a bright yellow. If it becomes brown it should be rejected as contaminated with fusel and empyreumatic oils, which have an injurious effect in dyeing.

Some dyers dissolve magenta in acetic acid, which takes it up very readily, but gives it a blue shade. A good method is to reduce the magenta crystals to fine powder, rub them well up with their own weight of alcohol, and allow the mixture to stand overnight in a closed vessel. In the morning the paste thus obtained is mixed with the smallest needful quantity of boiling water, boiled up for a few minutes and filtered into the dye pan through flannel.

Another method is to rub up the magenta in glycerine, and then boil in the smallest quantity of water needful to dissolve it, and filter for use. Glycerine is preferable to alcohol, because it does not evaporate, prevents "bronzing" on the surface of the tissues to be dyed, and has no "flattening" effect upon the colour. Indeed, were it not for its high price it would be largely added to the dye-bath in almost every case where aniline colours are employed

Magenta can also be dissolved in certain saline liquids, such as solutions of bicarbonate of soda, carbonate and bicarbonate of ammonia, and borax. These solutions dye redder shades than magenta dissolved in alcohol, glycerine, or water—an effect which can be, to some extent, also produced by adding a little white soap to the dye-bath. On the other hand, if it be desired to produce a more blue tone, a little tartaric or sulphuric acid is added.

In cotton dyeing a mordant is needed to cause the magenta to be firmly fixed upon the fibre. The selection is governed by the circumstances of the case.

If the article to be dyed consists entirely of cotton, whether in the state of yarn, or of a woven tissue, it may be prepared as for Turkey-red, or worked for a couple of hours in a decoction of commercial tannin, of good nut-galls, or of pale myrobalans,* or any other substance rich in tannin, but free from colouring matters. The cotton goods are then taken out of the tannin liquor, allowed to drain for a short time, and then worked in a weak solution of stannate of soda for about an hour. Next they are passed through water slightly acidulated with sulphuric acid, or with alum. They are then rinsed in pure water and worked in the magenta solution at ordinary temperatures to the shade required. Some dyers vary the order and apply the stannate of soda first and the solution of tannin afterwards.

Another process is to work the cotton yarn in a solution of the subacetate of lead, and afterwards in a solution of soap.

In piece-dyeing, where the weft is wool or worsted, and the warp cotton, a different procedure is necessary. The pieces are winced first in an infusion of gall-nuts or other similar material, and then in a solution of tin-crystals. The pieces are then rinsed in water and transferred to the colour-bath. Some dyers omit the tannin-bath lest it soil the wool, and others use instead of the tin-crystals a peculiar nitro-muriate of tin, which will be subsequently described as "Aniline Mordants."

In printing, magenta is applied to calico with albumen, and thickened with starch or gum. "Lactarine" (caseine) may also be used instead of albumen when no additional thickening is needed. In either case the goods after printing are steamed from thirty to sixty minutes.

Another method, invented by Schultz, is to mix ¼ litre of acetate of alumina at 10° of Baumé's hydrometer with 20 grms, arsenite of soda to every 4 grms, of magenta. This mixture is thickened with starch which has been boiled separately. The quantity of starch is increased the lighter the shade required. In printing this composition is mixed with the amount of colour required, and the goods are afterwards steamed.

The red in the accompanying pattern is magenta, fixed as above mentioned. The violet is Hofmann's (see below); the green, chrome-green, both fixed in the same manner as the magenta. The black is a so-called chrome-black, a mixture of logwood and bark-liquor, with chlorate of potash and acetate of chromium for mordant, thickened with starch and gum, and steamed.

Examination of Magentas.

The simplest method of testing a commercial sample of magenta, both for intensity and for purity of tone, is so dissolve a known weight in boiling

^{*} Contrary to an old prejudice, myrobalans are preferable to the best sumac, as they contain an oil which assists in the fixation of aniline colours.



MAGENTA.

water and to dye with the strained decoction a known weight of fine white woollen yarn or cloth. By thus comparing different samples, their respective tinctorial power can be readily ascertained, and the presence of tarry matters, unconverted aniline, &c., may be detected by the flatness and brownish cast of the colour. Sugar is sometimes used as an adulterant. This may be detected by treating the sample with concentrated alcohol. The magenta dissolves and is filtered off, whilst the sugar remains behind undissolved.

The following method is used to ascertain whether a magenta is a pure salt of rosaniline or is contaminated with mauvaniline, violaniline, chrysotoluidine, &c. The colour is dissolved in as little alcohol as possible, the solution diluted with its own bulk of water or rather more, and a drop is taken up by



PONCEAU.

means of a glass rod and applied to a piece of white blotting-paper. If more than one colouring matter is present the different shades will diffuse themselves in concentric circles and may be distinctly seen. This method is still more applicable to the aniline violets and blues, which are frequently heterogeneous.

Aniline Crimson.

The crude magenta-cake without any purification is sold under this name, and is used in dyeing certain maroons, browns, clarets, and other compound colours.

The colour, well bruised or broken up into powder, is placed in a suitable stoneware vessel and well stirred up with its own weight of hydrochloric acid. During this process the fumes given off should be carefully avoided. After the colour has steeped for a short time in the acid, boiling water is added sufficient to dissolve the whole. The solution thus obtained is carefully strained, and is then ready for use. To correct the acidity of the colour a small quantity of ammonia is added to the dye-bath. This preparation will in many cases supersede peachwood, producing brighter shades, with less trouble, and at a lower price. They are, however, more fugitive. Upon wool and silk aniline crimson, like magenta, is a substantive colour. Upon vegetable fibres it requires to be fixed with a mordant—generally a per-salt of tin—and an astringent.

Ponceau.

This is the trade name of an aniline colour manufactured by the eminent firm of Brooke, Simpson, and Spiller (late Simpson, Maule, and Nicholson). The process by which it is obtained is secret. The colour is redder than the reddest shade of roseine, appears exceedingly bright by artificial light, and is considered faster than the magentas. It is a substantive colour on wool and silk, the only precaution required in dyeing being to add the colour very gradually to the neutral bath, and work slowly up to the required shade. No previous mordanting or other preparation is necessary. The tone can, if needed, be varied by the addition of a little ammonia.

The aniline violets include a formidable list of colours, unlike in their preparation, constitution, and properties, and sold under such names as mauve, harmaline, parma, dahlia, primula, indisine, rosolane, violine, phenameine, &c.

Perkin's Violet, or Mauve.

The earliest aniline colour introduced into commerce has lost much of its importance. Runge had previously called attention to the violet colouration produced on treating aniline with chromic acid or the hypochlorites. In August, 1856, Mr. Perkin patented his process for the production of a violet colouring matter from aniline.

The production of this violet or mauve colour depends upon the action of oxidising agents upon aqueous solutions of salts of commercial aniline. The violet or mauve of commerce contains a powerful organic base now called *Mauveine*, soluble in alcohol, with a dingy violet colour. The development of the mauve is the result of the union of this base with an acid. The colouring matter generally used is the acetate of mauveine, a salt which may be obtained in fine crystals of a green metallic lustre. Mauveine has so great an affinity

188

for even the most feeble acids, that the dull colour of its alcoholic solution rapidly changes to purple under the influence of the carbonic acid of the breath. Mauveine is decolourised by nascent hydrogen, but its original colour is instantaneously restored by the oxygen of the air. The mauve of commerce is usually a brownish violet-coloured paste, very sparingly soluble in cold water, somewhat more so in hot water, but readily soluble in alcohol, woodspirit, aceton, in the acetic, sulphuric, hydrochloric, and tartaric acids, in glycerine and aniline. This substance may be obtained in crystalline form when its solutions are evaporated to dryness. The crystals exhibit, especially after having been washed with some ammoniacal water, a brilliant green colour. Mauve is precipitated from all its solutions by water, especially if the latter contains neutral alkaline salts, caustic alkalies, or metallic salts. If the paste or solid mass is placed upon a strongly-heated metallic plate red vapours are given off, and volatilisation appears to take place; but even in vacuo no sublimate is obtainable. When mauve is treated with rather concentrated hydrochloric or sulphuric acid it is converted into a blue-coloured mass, which a larger addition of acid renders green. On the addition of water the blue colour is first brought out again, and after a while the violet is restored. When mauve is boiled with dilute nitric acid there is formed a yellow-coloured liquid, and a reddish pulverulent mass scarcely soluble in water is precipitated. Chlorine water discolours the alcoholic solution, but its colour is restored by the action of sulphuric acid. According to M. Scheurer Kestner, the composition of mauve is represented by the formula C20H14N3, and it therefore only differs from rosaniline (C20H19N3) by containing less H. This view is not that of the celebrated discoverer of mauve, Mr. Perkin, who says that the material obtained by the action of bichromate of potassa upon sulphate of aniline is the sulphate of an entirely new base, mauveine, C₂₇H₂₄N₄. This base is prepared from the crystalline mauve of commerce by adding to its boiling solution a solution of caustic soda. By this proceeding the purple colour of the solution of the mauve changes directly to a violet blue, and when the solution is left standing a crystalline substance is deposited, which after having been first washed with alcohol, and next with water, exhibits after drying a brilliant blackish powder not unlike oligistic iron ore. Mauveine is soluble in alcohol, yielding a violet-coloured solution, which on the addition of an acid is converted into a purple colour. Mauveine is almost insoluble in ether and benzol, and is a strong base which even decomposes ammoniacal salts. When subjected to a high temperature decomposition takes place, and an oily basic substance is obtained distinct from aniline. Mauveine forms a series of salts, all of which have been carefully studied and described by Mr. Perkin, and which are nearly all rather hygroscopic. The salts of the mauveine, or indisine of commerce, are usually prepared by means of the oxidising action of suitable materials upon the salts of aniline of commerce (mixtures of aniline and toluidine) in aqueous solution. The method adopted for the preparation of mauve is as follows:—100 kilos. of heavy aniline are mixed with 54 kilos. of concentrated sulphuric acid and 2 kilos. of water. The acid thus diluted is added to the aniline little by little with constant stirring. When the whole has been poured in, the mixture is heated and stirred so as to obtain a homogeneous liquid, and is then allowed to cool. When cold add 140 kilos. of bichromate of potash dissolved in the smallest possible

quantity of water, and allow the reaction to proceed for twenty-four hours. The mixture becomes turbid, blackens, and at the end of the period has resolved itself into a clear liquid, and a black precipitate containing mauveine (indisine), chromic oxide, and certain resinous impurities. The large wooden vessels in which this process takes place are then filled up with boiling water. The whole is well stirred up and allowed to settle. The water, which contains thie excess of bichromate of potash and certain soluble impurities, is then carefully decanted off. The washing is thus repeated four times, and the bllack precipitate containing the colouring matter is then collected upon filters. It, is washed twice or thrice with water slightly acidulated with sulphuric acid amd then with cold water. The precipitate is then boiled with water in large vaats for three hours and often stirred. The liquid, which holds the colouring miatter in solution, is drawn off by decantation and filtration. This treatment is: repeated until nothing more can be dissolved. These aqueous solutions, mixed and filtered, are precipitated by an alkali or an alkaline salt. The prrecipitate, collected on a filter, is washed with luke-warm water to remove excess of the precipitating salt and a certain reddish colouring matter. It is finally converted into acetate of mauveine by the addition of the necessary quantity of acetic acid. To obtain the acetate pure, this process of solution. precipitation, and washing must be several times repeated. By this proceedure 100 kilos. of baraniline yield 75 to 90 kilos. of mauve in the state of thrick paste.

The selection of aniline is a very essential matter for the preparation of mrauve. The anilines suitable for it are not the same as those which give the beest results for magenta. The mauve prepared according to the process just described, though fit for practical purposes, is not chemically pure. If required in this state it must be boiled in a large quantity of water, and then filtered. Firom the solution the colouring matter is thrown down by means of an alkali. The precipitate thus obtained should be collected upon a filter, washed with water until free from alkali, and dried. When dry it is to be dissolved in absolute alcohol, the solution filtered, and then evaporated to dryness on a weater-bath. The mauve thus obtained is a brittle substance, with a beautiful bronzed surface; but if some of its alcoholic solution be evaporated on a glass plate, and viewed by transmitted light, it is of a fine bluish-violet. M.auve forms a remarkable compound with tannin. If an aqueous solution is mixed with a solution of tannin, precipitation takes place; the precimitate, after having been well washed, no longer possesses the properties of thee pure colouring matter, but is insoluble in water, and dissolves in concentraited sulphuric acid, forming a dirty green liquid; but on adding an excess of water to this solution the new compound is precipitated unchanged. With threse tannates dissolved in acetic acid, Messrs. Clift, Lowe, and Calvert dyed specimens of silk, wool, and cotton, which the latter gentleman exhibited earrly in the year 1858 before the Society of Arts.

Among the very large number of new methods proposed for the manufacture of this dye, especially after the spring of the year 1859, we may notice the following: – Messrs. Depouilly and Lauth's method (patented in June, 1860) consisted in adding to a salt of aniline a solution of chloride of lime, which yielded a purple insoluble precipitate. This was repeatedly washed in slightly acidulated water, dissolved in concentrated sulphuric acid, and re-precipitated by the

addition of an excess of water. It was then simply necessary to wash the precipitate thoroughly, in order to render it fit for use if dissolved in alcohol or methylated spirit. The chloride of lime process gives a more abundant yield than the bichromate method, but the tone of the violets obtained is redder and less pure. We may here mention that Mr. W. H. Perkin has lately succeeded in obtaining the product of Runge's experiment in the solid condition. He finds that it dissolves in alcohol, forming a solution of a nearly pure blue colour, which is changed to a brownish-red by the action of caustic alkali; it therefore differs essentially from the mauve, an alcoholic solution of which, if treated with caustic alkali, passes from purple to violet, The blue product, which the author proposes to call "Runge's blue," undergoes a very remarkable change when subjected to the action of heat. It is rapidly converted into a purple colouring matter, which is found to be the true mauve. Indeed Runge's blue is so prone to change into the more stable mauve that its composition cannot be satisfactorily determined. Mr. Kay, in January, 1860, took out a patent for producing purple-aniline,-most absurdly called "harmaline,"by adding to sulphate of aniline peroxide of manganese, and heating this mixture to 100°, when the "harmaline" so produced remained in solution, and was separated from an insoluble deposit. The dissolved colour was precipitated by adding to the solution ammonia in sufficient quantity to neutralise the acid, after which the insoluble colour was washed, dried, and dissolved in methylated alcohol. In January, 1860, Mr. Greville Williams patented the use of permanganate of potassa as a means of oxidising aniline and producing purples and other colours; at about the same time Mr. D. Price took out a patent for acting on sulphate of aniline by means of the peroxide of lead. In 1860 Dale and Caro patented the use of chloride of copper, in the proportion of 6 equivalents to 1 of a neutral salt of aniline. In place of chloride of copper, a mixture of sulphate of copper and common salt may be used in equivalent proportions. The quantity of water necessary to dissolve the mixture is added, and the whole is then boiled till a precipitate appears, which contains the colouring matter. At the expiration of three or four hours the process is completed. The precipitate is collected on a filter, and washed with a solution of soda or carbonate of soda so long as the washings contain chlorides. The residue is then extracted with boiling water so long as anything dissolves. The solutions thus obtained are filtered, and precipitated with a small quantity of soda or carbonate of soda. The colour thus obtained is ready for use. The matter insoluble in boiling water still contains a violet, which may be extracted by treatment with boiling dilute alcohol in a displacement apparatus.

On the 12th of January, 1861, another interesting process to obtain aniline purple was patented by M. A. Girard: pure aniline red (known as magenta) is mixed with an equal weight of aniline, and the mixture heated for several hours to 329° F., when the mass is changed to a fine purple colour, requiring only to be mixed with water and hydrochloric acid to remove any aniline or red dye in excess, leaving the purple insoluble; but on being well washed with water this becomes soluble in alcohol, acetic acid, wood naphtha, and boiling water, slightly acidulated with acetic acid. The French call this Violet Imperial.

In 1862 Mr. G. C. Nicholson secured a patent for producing a very beautiful

colour, named Regina purple. The following is a full description of his process:-"I take red dye, such as is made from aniline or its homologues, amd, without the admixture of either aniline or its homologue, I heat it carefully, in a suitable apparatus, to a temperature by preference between 300° and 420° F. The substance quickly assumes the appearance of a dark semi-solid mass, the red dye being transformed into a dark substance with evolution of ammonia. The mass I prefer afterwards to extract with acetic acid, using a quantity of aciid about equal in weight to the amount of the red dye treated, and this acid I dilute with enough alcohol to make a dye of convenient commercial strength: the solution obtained is of a deep violet or purple colour, and may be used directly for dyeing purposes. What I claim is the producing a violet or purple colour from red dye, such as is made from aniline or its homologues, by carefully treating it as described, without admixture either of aniline or its homologue." M. Stark patented a method of producing this colour, by boiling for two or three hours a mixture of a salt of aniline with red prussiate of pottassa, leaving the whole to cool, when a greyish-blue precipitate settles at the bottom. It is, however, not certain whether the colour thus obtained can compete with those already used. The use of the red prussiate of potassa for producing aniline purple had been mentioned by M. Emile Kopp before the datte of M. Stark's patent.

The paste violet (mauve) is tested for its tinctorial value in the following mainner: -3 grms. are exactly weighed, and dissolved in 50 c.c. of acetic acid. To this solution is added a quantity of 100 grms, of gum-water (containing 5000 grms, of gum to the litre), and next a quantity of 100 grms, of albumenwatter (containing 500 grms. of albumen to the litre). This mixture is used to print, by means of the roller, stripes on muslin. After the printing the stuff is diried, steamed, washed, and compared with a standard sample. This assay cam also be executed by a dyeing process in the following manner:—2 grms. of the paste are dissolved in 10 c.c. of alcohol (or methylated spirits), and diluted with water so as to yield a quantity of I litre; 50 c.c. of this liquid are taken, and diluted to a } litre. This fluid is brought to ebullition, and in it 5; grms. of wool are dyed, so as to exhaust the bath. The purples above meintioned, when fixed on woven tissues, are recognised by the following reactions, it being remembered that these colours can only be perhaps confused with the rosaniline violet and French purple (a peculiar orchil colour-to the former the Regina violet, just spoken of, belongs):—(1). When acted upon with strong mineral acids (sulphuric or hydrochloric) the dye in question turns blue. (2). Caustic alkalies do not act upon it in the cold. (3). A solution of sulphurous acld in water into which a piece of sheet zinc is placed causes the immediate decolouration of any tissue thus dyed.

A series of aniline violets, sold under a number of fanciful names, are obtained from rosaniline by the process of phenylation,—that is, one or two atoms of the hydrogen present in the rosaniline are replaced by the same number of equivalents of phenyl or of tolyl. The conversion of the red into a violet is effected in an enamelled iron retort, holding about 20 litres, heated in a paraiffin bath. The head is joined to the body by means of pressure-screws. The head is made high to promote the re-condensation of the aniline, which is violatilised. The retort is fitted with a mechanical stirrer, in the axis of which lies a tube through which steam can pass. The mixtures used vary in

proportion, according to the shade required. The more aniline is added the more hydrogen is replaced, and the more the violet produced inclines to a blue. The aniline employed should be as pure as possible. About equal weights of magenta and aniline are employed, according to the original specification of Girard and De Laire. The retort is raised to a temperature of 165° to 190° C., and maintained there till the process is complete, which may be in 60 to 90 minutes. The progress of the operation is observed by means of a rod inserted at an aperture arranged for the purpose. A drop of the contents being thus withdrawn is placed upon a white porcelain plate, mixed with a little alcohol and acetic acid, and its colour examined. The redder shade of violet is a mono-phenyl rosaniline, whilst the blue shade is diphenyl-rosaniline.

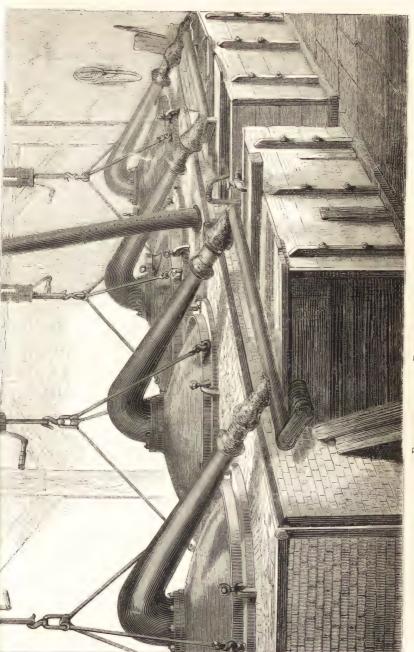
The process is varied slightly by different manufacturers. Levinstein mixes 3 parts of aniline with 1 of magenta, and maintains the whole for three or four hours at 180° C. A reddish shade is yielded by 100 parts magenta, 100 parts aniline, and 25 parts acetate of soda. As soon as the desired shade is obtained the contents of the retort are run out and heated with very dilute hydrochloric acid, which dissolves out any unconverted aniline that remains in the mixture. The violet colour is left floating on the surface of the liquid. It is strained off, freed from traces of acid by washing with water, dried, and powdered. The red-violet very much resembles solid magenta in appearance, but is less green. The bluer the violet the more of a coppery-red is its reflection. In the production of the very bluest violets soap is often employed. A favourite mixture is 100 parts aniline, 300 magenta, 75 acetate of soda, and 66 of a good curd soap. Prolonged heating, even with one and the same mixture, gives the result a bluer tone. The yield is greater than the weight of the magenta employed.

These violets are insoluble in water, either hot or cold. They dissolve in alcohol, wood-spirit, aceton, acetic acid, and concentrated glycerine. The use of these violets has very much diminished since the methylated and ethylated substitution-products of rosaniline—the so-called Hofmann and Paris violets—were discovered.

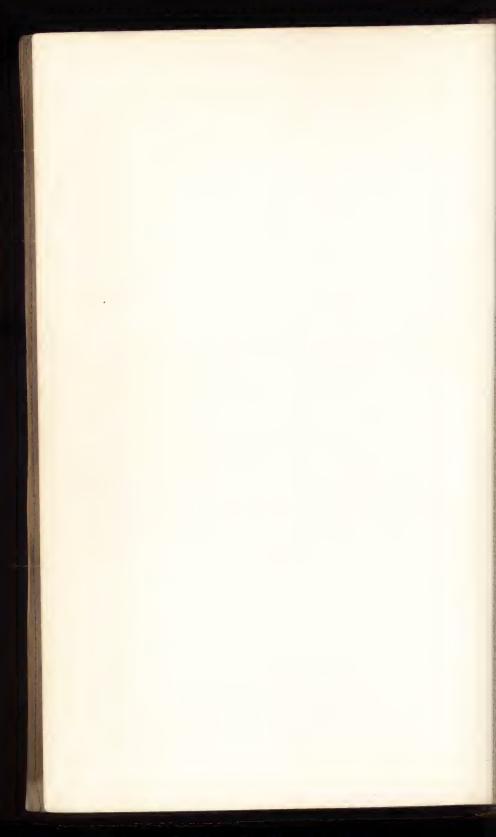
Of the Hofmann violets, chiefly manufactured by Messrs. Brooke, Simpson, and Spiller, there are a variety of shades, ranging from the reddest (R.R.R.) to the bluest (B.B.B.). These marks correspond to certain different grades of substitution, ethyl or methyl here taking the place of hydrogen, in the rosaniline atom for atom. The shade R.R.R. consists chiefly of monomethylated rosaniline, whilst B.B.B. is almost exclusively composed of trimethylated. The apparatus employed on the Continent in the manufacture of these colours is represented in Fig. 18. It is a boiler of enamelled iron, made strong enough to bear a pressure of 20 to 25 atmospheres, and varying in capacity from 80 to 100 litres. It may be heated either on the water-bath principle or by means of a steam-jacket. It is fitted up with a thermometer and a pressure-gauge.

For a red violet, "R.R.R.," the materials are --

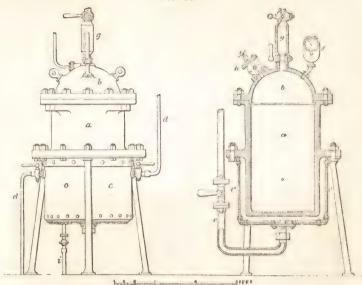
Rosaniline	 	 	To kilos.
Alcohol	 	 	100 litres.
Iodide of methyl or ethyl	 	 	8 kilos.
Hydrate of potassa or soda	 	 	10 .,



RETORTS FOR THE DISTILLATION OF METHYL-AMILINE.







Elevation and Section of the Apparatus.

a, b. Boiler and its cover. c. Steam-jacket, fed and emptied by the pipes d d.
f. Pressure-gauge. g. Cylinder, with two taps for introducing matters into the apparatus without diminishing pressure. h. Screw- or valve-tap, to permit the vapours to enter a warm condenser. i. Pipe to run off the steam-jacket.

The mixture is heated to 115° to 130° C., for about two hours. For a blue violet, "B" shade, the mixture is—

Rosaniline			 	 		 10	kilos.
Alcohol			 	 		 100	litres.
Iodide of n	nethy	/1	 	 	1.2	 5	kilos.
Iodide of e	thyl		 	 		 5	21
Potassa.			 	 		 TO	

For a bluer shade, "B.B."-

Rosaniline	 	 	 	10 kilos.
Iodide of methyl	 	 	 	20 ,,
Alcohol	 	 	 	100 litres.
Potassa	 	 	 	to kilos.

The alcoholic solutions of the iodides and of potassa are introduced in successive portions during the operation. When the required shade has been obtained the contents of the still are drawn off and purified. For this purpose the excess of alcohol is distilled off. The residue is then treated with an alcoholic solution of soda, in an apparatus fitted up with an agitator and a cohobator. It is then washed with boiling water in the same apparatus, with constant agitation, in order to remove both the alkaline iodide formed and the excess of soda. When thoroughly washed it is taken up in sulphuric,

hydrochloric, or acetic acid. The salt formed is dissolved in boiling water. The solution is then filtered, and precipitated by the addition of common salt. The pure colour is thus precipitated, and is collected on filters and dried. It is perfectly soluble in pure water, even at common temperatures.

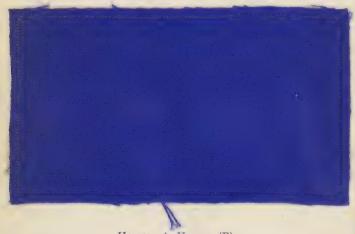
There are a variety of other analogous violets, as the mono-, di-, and trimethyl, and ethyl mauvanilines. They are prepared in a manner corresponding

to Hofmann's violets, and have a bluer shade.

The mono- and tri-methyl iodhydrates of trimethylated rosaniline are still more nearly blue.

Lauth and Grimaux have formed a violet by causing benzyl to replace the substitutionable hydrogen in rosaniline. There is also a methylic benzylic and a phenylic methylic violet.

Perkin's "Britannia violet" is prepared in a very similar manner, by treating 6 parts of rosaniline with 30 parts of methylic alcohol and 4 parts bromide of terebene.



HOFMANN'S VIOLET (B).

The comparative strength, shade, and brightness of a violet are best ascertained by dyeing patterns of known weight. Their pure or mixed nature may be tested by placing a drop of the solution upon blotting-paper, as directed for magenta. Instances occur where a violet consists of two portions,—the one soluble in water and of a red colour, and the other dissolving only in spirit. with a blue. Sometimes a considerable portion yields to no solvent employed in dyeing, and on examination proves to be quite valueless.

Aniline violets may be divided, as regards their application, into two classes—the insoluble (in water) and the soluble. The former are dissolved in methylated spirit, with the aid of heat, making the solution as strong as possible. The substitution of glycerine for a part of the spirit will be found to give very satisfactory results. Wood-spirit may be used in place of alcohol where very blue tones are desired. Great care must be taken in filtering the solutions. The soluble violets—those of Hofmann, Perkin's "Britannia," and the "Paris violet"—are readily soluble in water, and have a greater

affinity for cotton than most aniline colours. In some cases, where convenience requires highly concentrated solutions, these colours also are dissolved in alcohol, wood-spirit, or glycerine.

In dyeing the same general principles are observed as in case of magenta. In Hofmann's violets for wool and worsted the goods should be entered at 120° F., and the temperature be very gradually raised up to 212° F. Great care should be taken not to add an excess of colour, which is certain to produce flushing or bronzing. The annexed specimen is dyed with Hofmann's B., as prepared by Messrs. Brooke, Simpson, and Spiller. Cotton and mixed goods may be dyed as directed for magentas.

The following method of fixing the aniline colours upon cotton is due to Lloyd and Dale: To 41 litres of gum-water we add 240 to 300 grms. of pure dry tannin, and the colouring matter more or less according to the shade required. After printing and steaming at a pressure of about 50 to 75 grms. to the square centimetre, the pieces are then passed through a bath of tartrate of antimony or bitartrate of potash and antimony (tartar-emetic), containing 13½ grms. of this salt to the litre, and heated to 45° to 85° C. The goods are then rinsed and dried. A variation of the method is to print on the calico a thickened solution of tannin (133 grms. of tannin to a litre of gumwater for full, and 20 to 27 grms. for light shades). After printing, the pieces are steamed for an hour, and passed into the antimonial bath. They are next well washed and dyed in the colour-bath, which is slightly acidulated, and heated slowly to the boiling-point, at which it is maintained for twenty minutes. If after washing the white grounds are still faintly stained, they are bleached by being passed through a weak solution of chloride of lime, and afterwards through soap-lyes.

The addition of acids renders the tone more blue, but at the same time it deadens the colour and impairs its affinity for the fibre, especially in case of cotton.

ANILINE BLUES.

Paris Blue (Persoz, De Luynes, and Co.), Lyons Blue (Girard and De Laire), Mulhouse Blue (Gros-Renaud), Azurine (Calvert and Lowe), Azuline, Rosaniline Blue, Bleuine, Oxyphenylanilide, Dioxyphenylanilide, Night Blue, Methylaniline Blue, Triphenylic Rosaniline, Toluidine Blue, Rosotoluidine Blue, Opal Blue, Regina Blue, Nicholson Blue, Guernsey Blue.

Lauth observed on December 24th, 1860,* that when magenta, especially azaleine, is heated with a reducing agent, such as protochloride of tin, a purple and even a blue were obtained. In continuing these researches he observed that a blue matter could be easily obtained by heating azaleine with various organic compounds, such as aldehyde, several of the hydrurets of benzyl, acetyl, and many natural essences. This blue colour cannot resist the action of acids and of light, and is therefore practically useless. The action of aldehyde and the composition of the blue itself have been investigated by M. Willm, and are exhibited by the following formula:—

$$\underbrace{2(C_{36}H_{20}N_4O_4) + 5C_4H_4O_2 + 8HO}_{\text{Aldehyde.}} = \underbrace{3(C_{24}H_{11}NO_2) + 5C_4H_3(NH_4)O_4}_{\text{Blue, or Oxyphenylanilide.}} + \underbrace{3(C_{36}H_{20}N_4O_4) + 5C_4H_3(NH_4)O_4}_{\text{Oxyphenylanilide.}} + \underbrace{3(C_{24}H_{11}NO_2) + 5C_4H_3(NH_4)O_4}_{\text{Oxyphenylanilide.}} + \underbrace{3(C_{24}H_1NO_2) + 5C_4H_3($$

See vol. xxxi. of the "Bulletin de la Société Industrielle de Mulhouse."

Therefore the triamine azaleine has been transformed into a monamine blue, by a new chemical reaction; for aldehyde not only acts as a reducing agent, but converts a part of the nitrogen into ammonia. M. Lauth has also obtained a blue colour similar to the above by acting on methylaniline with bichromate of potassa. A blue also produced by the reduction of magenta, but resisting the action of acids and also of light, was patented by Girard in January, 1861, and is made by heating for several hours, at a temperature of 329° F., equal weights of magenta and aniline, and allowing the whole to cool; the substance produced is mixed with weak hydrochloric acid, which removes excess of aniline and red dye, and leaves a purple colour, which is further reduced into a blue colour by boiling it several times with a mixture of hydrochloric acid and alcohol. It is then washed with boiling water. The substance thus obtained is of a fine blue, with a coppery lustre. Bleu de Paris is another instance of the reduction of magenta into a purple and blue. It is prepared by heating for thirty hours, in a closed vessel, at a temperature of 356° F., I part of anhydrous bichloride of mercury with 2 parts of aniline. The mass is then treated with boiling water, and precipitated by the addition of common salt, this treatment being repeated several times until all traces of a green colour are removed. The blue thus produced resists the action of weak acids and alkalies, but assumes a red hue when acted on by these agents in a concentrated state. Sulphurous acid has no action, and it dyes animal fibres with facility. The formation of Bleu de Mulhouse is one of the most interesting reductions of aniline red, in a commercial point of view. It was invented by Messrs. Gros-Renaud and Schæffer: in I litre of boiling water they dissolve-50 grms. bleached shellac; 18 grms. carbonate of soda; 50 grms. of a solution of azaleine, made up of 125 grms. of azaleine dissolved in 1 litre of water and 1 litre of alcohol. The whole is kept at a boil for an hour, care being taken to maintain the fluid at its original bulk by the addition of

The most valuable and most scientific method of manufacturing aniline blue is that discovered by M. Marnas, of the firm Guinon, Marnas, and Bonnet, of Lyons, not only because it is based upon a novel chemical reaction, but also because the blue is produced directly from aniline, which is gradually oxidised into a blue by means of peonine. 5 parts of peonine are mixed with 8 parts of aniline, and the whole heated to the boiling-point for some hours, until nearly all the material is transformed into a blue colour, which is purified by successive washings; the first with boiling water, acidulated with sulphuric or hydrochloric acid; the second, with hot oils of tar; the third, with a diluted solution of caustic alkali; and the last with slightly acidulated water. The azuline, or Bleu de Lyons, so prepared presents itself as a reddish powder with a golden lustre, soluble in alcohol or methylated spirits. The solutions can be used for dyeing or printing. According to M. Willm, azuline is composed of C24H12NO4, which, in his opinion, may be considered as dioxyphenylamide, or—

 $N \begin{cases} C_{12}H_{5}O_{2} \\ C_{12}H_{5}O_{2} \\ H_{2} \end{cases}$

As regards the dark blue aniline colours resembling indigo, M. Fritzsche observed, during some of his researches on aniline, the production of a dark blue substance, which he prepared by mixing together equal volumes of a

solution of a salt of aniline and alcohol, and adding to this another solution containing chlorate of potassa and hydrochloric acid: after a short time a dark indigo-blue precipitate is produced, which, when washed with water, may be dried and preserved. This colour is not practically available for dyeing, owing to its insolubility. Dr. Hofmann also produced this colour by acting on a solution of hydrochlorate of aniline with a solution of hypochloric acid. Messrs. Clift, Lowe, and Calvert, of Manchester, also produced it by acting on hydrochlorate of aniline with chlorate of potassa. M. Willm has also obtained this peculiar blue by mixing the sesquichloride of iron with nitrate of aniline: after a short time a chemical action sets in, when the liquor becomes purple, from which is gradually deposited the blue colouring matter. The same reaction is obtained by substituting bichromate of potassa for the chloride of iron. According to this same author, this blue is also procured when a salt of aniline is mixed with red prussiate of potassa, but the blue produced in this instance is soluble in alcohol, which is not the case with the other varieties. These blues resist all chemical agents excepting acids, which turn them green. This is the only drawback to their employment as substitutes for indigo, but notwithstanding this defect they are applied in calicoprinting for producing greens, blues similar to indigo, and blues and greens so dark as to appear black.

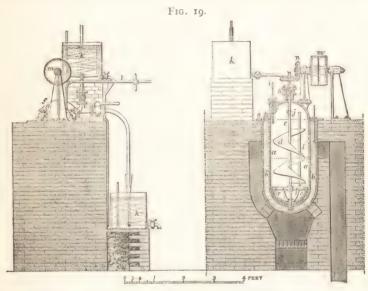
Some of the most important aniline blues are made by phenylation, in a manner similar to what has been already described under aniline violets. The apparatus employed is a retort of enamelled cast-iron, of the capacity of about 20 litres, and heated by means of a paraffin-bath. It is composed of two pieces, the neck and the cylinder, united by means of pressure-screws. To the neck of the retort are adapted a receiver and a cohobator, the latter serving to maintain the same excess of aniline to the conclusion of the process. The retort is fitted with a mechanical agitator, whose axis moves in a tube serving as a passage for a current of steam. (See Fig. 19.) Into this apparatus are introduced—

Heat is then applied, and the temperature is kept close upon 170° C., by means of a thermometer plunged in the retort. The operation lasts about two hours, its progress being judged by withdrawing successively small portions with a rod, and dissolving them in alcohol and acetic acid upon a piece of white porcelain. The spot ought to be entirely and purely blue. If there is a too decided red halo round the streak the operation is not complete. If the halo is of a sallow, brown, or greyish-green tint, the process has been carried too far. In a well-managed operation the blue should remain dissolved in the excess of aniline, and when the reaction is over the mass should appear semifluid, but perfectly homogeneous. The retort is then raised up by means of pulleys, and the screws which secure its head to the boiler are undone, so that the contents may be poured out.

The crude mass is treated differently, according to the kind of colour desired. For the common blues, all that is required is the separation of the blue from the excess of aniline. One method for attaining this object consists in sweeping the aniline mechanically away by a current of steam. In the other method it is removed by washing with dilute acids. The residue is then fit for sale.

Refined Blues are obtained by various methods. The crude product is mixed with alcohol, and poured in thin streams into water acidulated with hydrochloric acid. There is formed a salt of aniline, which remains in solution along with any excess of unconverted rosaniline, and the blue is precipitated. It is then collected on a filter, and repeatedly washed with boiling acidulated water.

Night blue, so called because it preserves its tone by artificial light, is simply a salt of triphenylic rosaniline, perfectly pure. To prepare it, the refined blue resulting from the last operation is repeatedly washed with cold alcohol, and then dissolved in boiling alcohol, after having been finely



Apparatus for the Preparation of Aniline Blue.

a. Retort of enamelled cast-iron, immersed in the oil-bath, b. c. Vertical shaft, carrying two agitators, the one d, a spiral, and the other fitted with wings parallel to the sides of the retort, and with teeth extending very nearly to the bottom. f. Cover fitted on to the retort by the pressure-screws, g, and carrying h, a stuffing-box for the shaft c; another, i, for the thermometer and a tubulure, j, communicating at will by means of cocks with a worm, k, or a worm cohobator, k', and l, a tube for introducing steam into the apparatus. The steam may be otherwise introduced by having a hollow shaft for the agitator in place of a solid one. Movement is given by the pullies, m m, and the cog-wheels, n n.

powdered. The mixture is then filtered, and mixed with an alcoholic solution of caustic soda, when the blue is entirely thrown down as a base. When the whole is cold the colour is collected on a filter, washed repeatedly with boiling water, and then treated with a sufficient quantity of the acid intended to form a salt.

Another method is to dissolve the refined blue, in a mixture of alcohol and hydrochloric acid, in double-bottomed retorts enamelled within. The mixture is boiled, when a part of the alcohol distils off, and it is then allowed to cool.

As the pure hydrochlorate of triphenylic rosaniline is less soluble than the accompanying impurities, it is dissolved last and re-deposited first, and is separated from the liquid. By repeating this treatment several times the blue can be obtained pure.

The mother-liquors are carefully collected, and distilled over lime. Alcohol passes over first, then aniline, whilst the colouring matters remain along with the lime. We shall still briefly describe some of the procedures used to obtain the shades of blue known in commerce as B., B.B., B.B., &c.

The first of these shades is produced by heating, in the apparatus Fig. 19, the subjoined mixture, to the temperature of 180° C., for about two hours:—

2 kilos. pure rosaniline;

3 kilos. pure aniline, distilling at 182° to 185°, and free from hydrocarbons. 270 grs. crystallisable acetic or benzoic acid.

The choice of these two acids is not indifferent. Acetic acid furnishes colours better adapted for wool, and benzoic for silk.

When the colour is found, by the trial method above described, to have reached the proper shade, the retorts are emptied into a wooden vessel containing 10 kilos. of concentrated hydrochloric acid, constantly stirring. The whole is then filtered, and the residue pressed, washed in a large amount of water acidulated with hydrochloric acid, and kept at the boiling-point by blowing in steam. This treatment is continued until the blue is quite reduced to a powder. It is then filtered and pressed again. The yield is 3½ kilos. of dry blue.

The preparation of the shade B.B. is quite similar, but the amount of aniline used is increased from 3 kilos. to 5. To purify the result, the contents of the retort are poured into a vessel of enamelled cast-iron, surrounded by cold water, to stop further reaction. When the product is cooled down to 150° add 7 or 8 kilos. of concentrated alcohol, and stir till the whole is perfectly homogeneous. The apparatus is then placed in a water-bath, and heated till the alcohol begins to boil. It is then taken from the water-bath, allowed to cool, and the colour precipitated by adding—with constant stirring—10 to 12 kilos. of hydrochloric acid. The whole is then filtered, always at the same temperature of 45° if constant results are aimed at; the product is pressed, washed in abundance of water, and dried. The yield is 1 kilo. 325 grms. of B.B.

To obtain B.B.B., take I kilo. of B.B., finely ground and quite dry, I kilo. of alcohol, and 2 kilos. of aniline, and heat the mixture in the waterbath, with continued agitation till the mixture is uniform. The viscid liquid resulting is then poured into 25 kilos. of alcohol, and heated to boiling, when 2 kilos. of an alcoholic solution of soda are added, containing 20 per cent of alkali. The solution is filtered, precipitated with a slight excess of hydrochloric acid, allowed to settle for forty-eight hours, filtered, drained, and the residue pressed. The blue obtained is washed with boiling water slightly acidulated, collected, and dried. One kilo. of B.B. yields thus about 800 grms. of B.B.B.

Soluble Blues.—The aniline blues hitherto described have the inconvenience of being soluble only in alcohol. The analogy existing between triphenylic rosaniline and indigo suggested the use of sulphuric acid. In 1862 Nicholson succeeded in obtaining a true sulpho-conjugate acid of triphenylic

rosaniline, analogous to the sulphindigotic. In the preparation of the earlier soluble blues a very large proportion of sulphuric acid was employed. The mixture was—

The ingredients are mixed at once, and the reaction accelerated by means of heat. The temperature is raised, by means of a steam-jacket, to 130° or 140° C., but must never pass 150°. When the mass is homogeneous, and when a drop of the acid blue gives a complete and clear solution in ammonia, the reaction is over. The mass is allowed to cool, and poured by slow degrees into 8 to 10 times its weight of water, with constant stirring. The blue is thrown down in a state of fine division, which is filtered and washed till the water begins to take a blue colour, showing that the mass is no longer acid, the coupled blue sulpho-acid being insoluble in dilute acids, though soluble in pure water. It is then dried in any convenient manner. When dry it is put in a cast-iron vessel enamelled within, mixed with a slight excess of ammonia, and heated. The coloured salt floats on the surface as a golden-bronzy layer. It is collected, broken up, dried, and powdered, and is now ready for use. The more recent method of preparing soluble blues differs in employing a smaller proportion of sulphuric acid, and in keeping the temperature below 100° C. One kilo. of B.B. blue is finely powdered, and added by degrees to 3 litres of concentrated sulphuric acid, and the mixture is kept at the temperature of the water-bath till a drop thrown into water gives a blue precipitate, which is washed by decantation. The precipitate thus purified and freed from acid should not colour water, and should dissolve without residue in aqueous solutions of soda or ammonia. The whole mass is then poured into 30 litres of water, constantly stirring,—an operation performed in wooden vats hooped with wood. The whole is allowed to settle for twenty-four hours, and is filtered through stout flannel. The precipitate, when it ceases to drop, is pressed. The pressed residue is heated in the water-bath with hydrate of soda till all the mass is dissolved. The neutralisation of the soda should be as exact as possible. The blue is then allowed to dry on enamelled plates, in a hot chamber, powdered, and mixed with 20 per cent of crystalline carbonate of

Nicholson blue and Guernsey blue are manufactured by Messrs. Brooke, Simpson, and Spiller, and have the advantage of ready solubility in water, combined with a greater degree of fastness than most aniline colours can offer. The exact method of their preparation has not been made public.

In dissolving and dyeing with aniline blues, a variety of processes are employed. The ordinary blues, as we have already intimated, are insoluble in water, and can be brought into solution by the use of alcohol or wood-spirit.* The purer a blue, the more alcohol is required for its solution, and the greater difficulty is experienced in fixing it upon cotton. The common blues are prepared for use by boiling in alcohol sufficient to take them up, and then very carefully straining. They dye wool and silk without mordants, the former at

^{*} It may be useful to point out a distinction often overlooked. Methylated spirit is common alcohol mixed with a small percentage of wood-spirit, which latter is otherwise known as methylic alcohol or wood-naphtha.

high and the latter at a low temperature. Sulphuric acid, or in case of silk tartaric acid, may be added to the dye-bath with advantage.

The opal blues are still less soluble. They should be ground to a very fine powder, and well rubbed together with sulphuric acid sufficient to moisten the colour. The acid employed should be perfectly free from lead and from nitrogen compounds. Alcohol is then added, sufficient to dissolve the whole. The mixture is raised to the boiling-point, and maintained at that temperature till all is dissolved. The liquid is then very carefully filtered.

For cotton these blues have no affinity, and the attempts to fix them upon that fibre in dyeing have not been very successful. In printing they may be fixed by means of albumen or lactarine, as described under Magenta. The following modification of Perkin's process may be successfully used for blues, as well as for all aniline colours whose colouring principle is a base. Arsenious acid is dissolved in pure glycerine to saturation. To each gallon of the thickened aniline colour from one-eighth to one-fourth part of this solution is added, together with an equivalent amount of acetate of alumina. The colour is then printed upon calico, bleached as for madder, and steamed at a pressure of about I lb. per square inch for some three-quarters of an hour. The glycerine is thus dissipated, and an insoluble compound of arsenite of alumina and of the coloured base is produced in the fibre of the cloth. After steaming, the colours are not, as a rule, very bright, but may be rendered so by treatment with boiling soap-lye for half an hour. It seems probable that in this soaping a portion of the arsenite of alumina is decomposed, with the production of a corresponding amount of stearate or oleate—the stearates and oleates of the aniline bases, and their double salts; but no direct use seems as yet to have been made of them in dyeing cotton, if we may except the following process, which finds a limited application in skein-dyeing. The cotton skeins are first dipped or worked in a solution of alum, and after being well squeezed out or dried they are worked in a bath of soap-lyes. They then take up aniline colours with great facility, but the combination between the fibre and colouring matter is not very stable so far as washing in soap is concerned, though the colours resist light fairly.

In dyeing piece-goods made of a mixture of animal and vegetable fibre,—such as delaines, coburgs, &c.,—the worsted is first made to take an aniline blue in the ordinary manner. The cotton-warp is then dyed a very bright Prussian blue, with "blue-iron" (see chapter on Mordants) and ferrocyanide of potassium. Several mordants have been tried for fixing the aniline blue upon the cotton. Amongst others, the nitrate of sesquioxide of chrome enables the aniline blues to lay a firm hold upon the cotton, but unfortunately at the same time it injures the brightness and purity of the colour already deposited upon the wool or worsted, turning it do a dull purple or slate.

The Nicholson and Guernsey blues are dyed as follows:—For woollen piece-goods the bath is made alkaline with soda, borax, or silicate of potash. The colour is then added very gradually. The goods are entered at about 120° F., and worked up slowly to just below the boiling-point, at which the bath is kept for twenty minutes or half an hour, according to the shade required. The cloth is then taken out, washed well in cold water, and worked in a bath slightly acidulated with sulphuric acid, in order to develope the colour. The pieces are finally washed in cold water. In order to ascertain

whether the required shade has been reached, several bits of waste material of a similar kind are tacked on to the goods being dyed. From time to time one of these is taken off, rinsed in water, steeped for a moment in dilute acid in order to try the shade. The accompanying specimen of Nicholson's blue (4 B) we owe to the courtesy of the firm of Brooke, Simpson, and Spiller.

Guernsey blue is a very permanent colour, and is frequently applied upon a ground of cam-wood or santal-wood, in order to produce a cheap and permanent shade resembling a vat-blue.

ANILINE GREENS.

Usebe Green, Cherpin Green, Emeraldine, Night Green, Rosaline Green, Emerald-Green, Aldehyde Green, Iodine Green, Ethyl-rosaniline Green, Picrate of Ethyl-rosaniline, Sexethyl-rosaniline, Iodide of Ethyl Green, Pomona Green, &c.

The earliest aniline green introduced was the emeraldine of Messrs. Lowe, Clift, and Calvert, which was not prepared as a separate dye, but produced on the fibre. To print with this colour, 500 grms. of chlorate of potash were dissolved, with the aid of heat, in 25 to 30 grms. of starch liquor. When the mixture was cool, 1½ kilos, of the acid chloride of aniline (or of one of its homologues), containing 500 grms. of aniline, was carefully incorporated. The colour was developed by exposing the printed goods to the air for twelve to eighteen hours. The process has now merely a historical interest.

Iodine Green, or Bimethyl-Iodhydrate of Trimethylic Rosaniline.

This is obtained, in greater or less quantity, in the preparation of Hofmann's violet. Tillmanns, Meister Lucius, and Brüning, all made more or less successful attempts at its manufacture in 1865. In the same year Wanklyn patented a process for its production, which became the starting-point for the present successful methods.

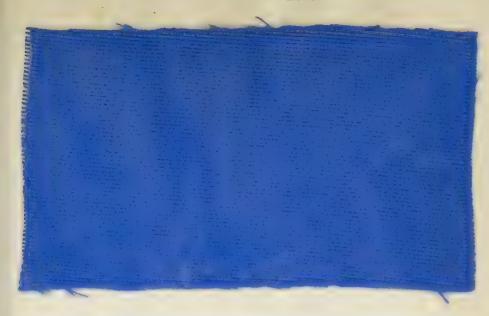
It is now manufactured in air-tight vessels of enamelled iron, of the capacity of 80 to 100 litres, and capable of bearing a pressure of 25 atmospheres. They are heated by means of a steam-jacket (Fig. 20). As the green begins to decompose at 110° C., it is necessary to know exactly the temperature of the steam circulating in the steam-jacket, which is therefore fitted with a pressure-gauge. In the head of the vessel is adapted another, to indicate the pressure existing in the interior of the apparatus. There is also a screw-tap, by which, at any given moment, the excess of the reagents employed, or of the liquid products of the reaction, may be distilled off. The ingredients used are—

10 kilos. of pure acetate of rosaniline;

20 ,, pure iodide of methyl;

20 ,, methylic alcohol, boiling at 64° to 70° C.

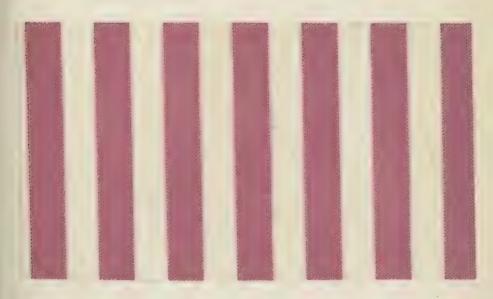
Steam is now turned on, taking care that during the whole operation the pressure in the steam-jacket may not exceed I atmosphere. In the interior of the boiler the pressure rises rapidly to 8 atmospheres, and then more gradually to 10 or II, which it must not be allowed to exceed. The process lasts four to five hours. At the expiration of that time the steam is turned off, and the apparatus allowed to cool. The pressure falls by degrees, and after twelve



Nicholson's Blue (4 B.)

hours it still amounts to 4 atmospheres. A tube is then fixed to the screwtap, which leads to a worm, communicating with a series of large globes, and the distillation is begun.

When the distillation is at an end the boiler is opened, and the semi-fluid contents are drawn out, and put to dissolve in a boiler containing 600 litres of distilled water and fitted with a steam-jacket. The green dissolves entirely, whilst the violet matters remain insoluble, with the exception of a small quantity which is kept in solution by the acid set free during the reaction. This residue is removed by a first filtration. To the filtrate about 35 kilos. of common salt are added; the boiling is continued, and the free acid is neutralised by crystalline carbonate of soda. To regulate the quantity, a

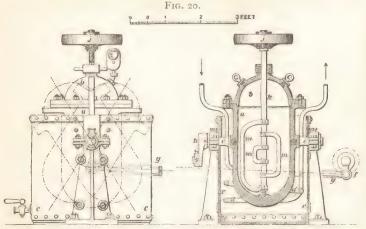


SAFFRANINE PINK.

small portion of the liquid is taken and filtered over sand. When the filtrate runs through a fine green, without any mixture of blue or violet, the addition of carbonate of soda ceases, 1½ to 1¾ kilos. of crystals being generally sufficient. The whole liquid, when cold, is now filtered over sand, to remove blue and violet matters. The filtrate is precipitated by a cold saturated solution of perfectly pure picric acid. For the proportions taken, 3.46 kilos. of picric acid will be required. The picrate formed is but sparingly soluble in water, and is consequently thrown upon a common filter and slightly washed. The precipitate is a very fine paste. It is allowed to drain till sufficiently concentrated. The dyer is obliged to make use of a small proportion of alcohol in dissolving this green.

Soluble Green.

In preparing this colour we substitute for the picric acid the sulphate, chloride, or acetate of zinc; there are thus obtained double salts of zinc, and of the



a b. Boiler and lid. c. Bath, containing water heated by steam circulating in the worm, d. An oscillatory movement on the trunnions, c, is given to the boiler by the excentric, f, the crank, g, and the handle, k. This oscillatory movement may be replaced by an internal agitation of the contents by means of the pulley, j, the shaft, k, and the paddles, m.

dimethyl-hydriodate of trimethyl-rosaniline. These compounds are soluble in water, and of a less yellow tone than the picrate. They are sold in the dry state.

The yield of the process should be about 60 per cent of green and 40 of violet, which can be transformed into green as follows:—The violet is well washed with water, dried, and powdered. It is then dissolved in pure alcohol (free from methylic spirit), and its base is liberated by the addition of caustic soda. It is then put in a suitable apparatus, provided with an agitator and a cohobator. An equivalent weight of methylic iodide is added, and the apparatus is carefully heated in the water-bath, so as not to exceed 48° C. As soon as the conversion is over, which is very rapid, the whole is quickly cooled, acetic acid is added, and the contents are poured into a large wooden vat containing hot water. The green is separated from residual traces of violet

by means of common salt and soda crystals; the filtrate is precipitated with common salt, and the precipitate collected and dried. The green prepared in this manner is generally finer than that made directly from rosaniline.

Crystalline Green.

To obtain the green in a pure crystalline state the crude product is poured into a very small quantity of boiling water,—about 60 litres for an operation made with 5 kilos. of acetate of rosaniline. In separating the green from the violet, soda crystals are used more freely, even at the risk of destroying a part of the green. The boiling filtrate, on cooling, deposits fine green needles on the copper rods suspended in the crystallising vat, whilst a crust of less pure crystals settles at the bottom. These crystals are washed slightly with water and dried.

Aldehyde Green.

This colour was discovered by Cherpin in 1862. Its chemical constitution is still unknown. Hofmann's analysis shows it to consist of $C_{22}H_{27}N_3S_2O$. For its preparation 1 kilo. of rosaniline is dissolved in 2 kilos. of sulphuric acid, of sp. gr. 1.63, previously mixed with 500 grms. of water. When the solution is homogeneous, it is mixed with 4 kilos. of a concentrated alcoholic solution of aldehyde, added in successive portions. The reaction is complete in about twenty minutes. The mixture is poured into 25 litres of water, in which 4 kilos. of hyposulphite of soda have been previously dissolved. The liquid is boiled seven or eight minutes, and filtered. The green is found in solution, and is thrown down by means of tannin, acetate of soda, or a salt of zinc along with an alkali. The green is washed with water to remove organic salts, re-dissolved in alcohol, and precipitated with ether. This green yields beautiful shades in dyeing and printing, but is always prepared by the consumer when wanted, as it spoils on keeping.

In dyeing with greens sold as insoluble tannates, it is necessary to dissolve in water acidulated with sulphuric acid. In this solution wool and silk are dyed, the former at a higher temperature than the latter.

On wool very full shades may be obtained with iodine green by the following process recommended by Dale. The wool is simply worked in very dilute hypochlorite of lime (bleaching-lime), and is then found to take up the colour very readily.

The so-called pomona paste of commerce dissolves freely in water without alcohol. It is worked upon wool as follows:—A bath of warm water is prepared at 158° F., to which silicate of potash is added sufficient to give the water a greasy feel. In this the wool or woollen yarn is worked to saturation. The colour, which has been in the meantime separately dissolved in some cold water, is now very gradually added to the above bath, the wool being still worked till a bit taken out—and passed through some water acidulated with acetic acid—shows the right shade. The whole is then taken out and put in a separate bath of water, at 158° F., soured with acetic acid. A little commercial tannin or extract of galls may be added to fasten the colour. If the shade is not sufficiently yellow, picric acid is added to the last bath.

Cotton is first well worked in sumach, galls, or myrobalans; then in double muriate of tin. It is next rinsed in water, and worked in the colour dissolved in cold water.

In printing, Sevez recommends the following process:-

The mixture is heated in the water-bath to dissolve the salt, and then allowed to stand for three or four days. At the end of this time it is used for printing. The colour will bear steaming, but the result is less satisfactory upon calico than upon silk and worsted.

Rosanaphthylamine, or Naphthylamine Red.

To prepare this beautiful colour, introduce into a glass flask, capable of holding 10 litres,—

3 kilos. of azonaphthyldiamine, in powder;

3 ,, naphthylamine, in powder;

21 . crystalline acetic acid.

The flask is now heated in the sand-bath until the mixture is completely dissolved, but care is taken to keep the temperature between 160° and 180° C. The red colouring matter is developed by degrees, and at the same time ammonia is given off. The operator must watch lest the colour should pass on into a violet, and stop the operation as soon as the slightest violet colouration appears. At this instant 150 or 200 grms, of crystallisable acetic acid are added; the flask is removed from the sand-bath, and the contents are poured out upon plates of sheet- or cast-iron. The crude matter thus obtained contains, besides rosanaphthylamine, acetate of naphthylamine, violet colours, and other secondary products. To purify the rosanaphthylamine, 10 kilos, of the crude matter are treated with 500 litres of water, acidulated with hydrochloric acid. When the solution is complete, and the liquid saturated, it is carefully filtered through woollen cloth. The filtrate is exactly neutralised with carbonate of soda, and mixed with common salt in excess. Hydrochlorate of rosanaphthylamine is thrown down in a crystallised state. The crystals are purified by two or three successive solutions in acidulated water and precipitations with common salt, and are then sufficiently pure for dyeing.

The colour produces bright rose shades, with a peculiar reflection which renders it valuable for dyeing silks and velvets.

Geranosine.

This beautiful ponceau red, first prepared by Luthringer, is a product of the oxidation of rosaniline, and is possibly one of the stages of transition from rosaniline to rosolic acid.

For its preparation 1 kilo, of any salt of rosaniline is dissolved in 1000 litres of boiling water, and the solution is allowed to cool down to 45° C.

On the other hand, $4\frac{1}{2}$ kilos. of the nitrite of barium or calcium, or of peroxide of barium or calcium, are dissolved in 35 litres of cold water. The two liquids are then mixed, and 10 kilos. of the strongest sulphuric acid are added. The solution becomes at once a lemon-yellow, and after a few moments it is quite colourless. The sulphate of baryta precipitated is filtered off, and the temperature of the mixture is progressively raised to 100°. By degrees the liquid begins to assume an intense red, and after boiling for two

minutes the reaction is complete. The liquid, when cold, is mixed with chloride of sodium, and the geranosime precipitated is collected on filters. The colour is soluble in water, and especially in alcohol. It is not decolourised by ammonia. Acids make the shades brighter.

Saffranine.

This is a colouring matter of a bright red rose, resembling carthamine. It is produced by the action of nitrites upon heavy anilines: 2 parts of baraniline are heated for five or six minutes to 80° to 100° C., with 1 part of arsenic acid and 1 part of a metallic nitrite, when a coloured mass is obtained which is treated with boiling water. The solution is neutralised with an alkali. The intensely red liquid is filtered, and precipitated with common salt. The precipitate, filtered and drained, is sold as a paste. Saffranine is also producible by the action of chromic acid.

The shade of specimen is produced by mixing I gill of saffranine paste with 20 gills of the subjoined thickening:—I gallon of acetate of alumina standard, I gallon of water, 2 lbs. of starch. Boil, cool, and add I pint of arsenic and glycerine standard.

The "Acetate of Alumina Standard" is made with:—I gallon of boiling water, 2½ lbs. of alum. Dissolve, and add 3 lbs. of white acetate of lead. Dissolve, let settle, and use the clear liquid.

The "Arsenic and Glycerine Standard":—I gallon glycerine, 4 lbs. arsenious acid. Boil till dissolved, and filter.

After the saffranine colour has been printed on the goods are steamed for thirty minutes.

Phœnicine.

This is another fine red colouring matter, discovered by Willm in 1861, and prepared by boiling an acetic solution of mauveine with binoxide of barium. The ponceau shade is quickly developed. The boiling is then stopped, and the excess of acetic acid is exactly neutralised with a standard solution of carbonate of soda. Carbonate of baryta is added, the mixture is filtered, and phænicine remains in the filtrate. It may be thrown down by the addition of common salt.

Phoenicine may be analogous to the geranosine of Luthringer. It may possibly be identical with the ponceau colour described by Delvaux. He dissolves r part of chromic acid in 18 to 20 parts of water, and adds r part of aniline. After standing for some hours a blackish precipitate is formed, which is filtered off, while the liquid retains a yellowish-brown colour. The precipitate on treatment with boiling water yields a liquid which dyes silk or wool of a reddish-violet. If rendered alkaline with ammonia the violet colour is thrown down, and the red or ponceau remains in solution.

ANILINE BROWNS.

A maroon-brown was patented by Girard and De Laire in 1863: they take 4 parts by weight of anhydrous hydrochlorate of aniline, and 1 part of dry magenta (not an acetate), which is put in as soon as the hydrochlorate melts. When the magenta is perfectly dissolved the heat is raised to 240° C., and maintained until the colour—which was at first of a reddish violet—suddenly becomes a maroon. The process lasts one hour or two, and its approaching

termination is known by the appearance of yellow fumes, which condense in the cold parts of the apparatus, whilst an alliaceous odour becomes recognisable. The maroon-brown matter thus obtained is soluble in water, alcohol, and acids. The aqueous solution is employed at once in dyeing, without preliminary treatment. It may, if required, be purified by precipitation with common salt. The so-called naphtha-brown is merely the crude melt from the manufacture of magenta, containing consequently the secondary products and undecomposed aniline. Sieberg prepares a brown from the colouring matters precipitated from the mother-liquors resulting from the manufacture of magenta. He heats I part of hydrochlorate of aniline up to the point of fusion, and adds then } part of the colouring matter just mentioned, the apparatus being set in a sand-bath until the brown colour is developed. The product is mixed with 2 parts of carbonate of soda crystals and 25 litres of hot water, and is well stirred and mixed up. The solution is then decanted, and the brown is repeatedly washed with water. In this state it presents the appearance of a brownish-black tarry mass: 5 kilos. of this crude mass are dissolved in 45 litres of alcohol; 65 litres of water are added, with constant stirring. The clear liquid, after settling, is ready for use.

Another brown colour is met with in commerce, obtained by causing metallic tin and hydrochloric acid to react upon binitro-benzine, and treating the

resulting mass with an alkaline or metallic nitrite.

Schultz prepares a garnet-brown by causing hyponitric acid to react upon a salt of rosaniline. A variety of brown matters may be obtained by oxidising rosaniline or leukaniline by means of chlorate of potassa, peroxide of lead, bichromate of potassa, &c.

Jacobsen's brown is made by introducing into a capacious flask I part of picric acid and 2 parts of commercial aniline. The mixture heats, and the . picric acid dissolves to a thick liquid of an orange-yellow, a result which is promoted by stirring and the application of a gentle heat. When the temperature is raised to 110° to 120° the mass grows brown, and throws off abundant vapours. To avoid boiling over, the temperature is kept at 140°, or at the utmost not above 160° C., for some hours, as long as ammoniacal fumes are given off. The process is at an end when a small portion taken out of the flask and thrown into water gives only a very feeble yellow tint to the liquid. The black mass is then poured, with constant stirring, into water strongly acidulated with hydrochloric acid, and boiled repeatedly in successive portions of water to remove any undecomposed aniline. It is still better to grind up the mass before allowing it to boil, and again after the liquid has cooled, to facilitate the removal of a red colouring matter. The residue, after boiling, is collected upon a filter, and well washed, first in a dilute solution of soda, and then in pure water. If the temperature has not been raised too high, the mass is entirely soluble in alcohol. For use it is dissolved in alcohol, acidulated with sulphuric acid and mixed with glycerine. It dyes silk and wool without mordant, the former a Corinth red, and the latter a black-brown with a violet reflection.

The crude colour may also be purified by adding it to concentrated sulphuric acid. After some time the sulphuric solution is poured into water, and the pure colour is precipitated by the addition of common salt. In this state it is more readily soluble in alcohol.

The aniline browns are generally dissolved in boiling water, and used directly for dyeing. In case of wool and silk no mordant is required. Upon cotton they are fixed by processes similar to those already indicated for other aniline colours. The shades produced can be modified at discretion by the addition of acids to the dye-bath, or of magenta in larger or smaller amount.

In printing, a garnet-brown may be produced upon the fibre by the following process, due to Keechlin:—

Solution of	magenta,	50	grms	. to	a lit	re of	alcohol	 25 centilitres.
Gum-water								 75 ,,
Oxalic acid								 50 grms.
Chlorate of	potassa							 25 ,,

By adding successively increasing doses of neutral extract of indigo, the shade may be modified up to a black. If a redder garnet is required the proportions of oxalic acid and of chlorate of potassa should be diminished. For a yellower shade any yellow lake may be added to the colour, provided it does not contain oxide of tin for its base.

ANILINE YELLOWS AND ORANGES.

Chrysaniline, or phosphine, was discovered by Nicholson, and is manufactured by the firm of Brooke, Simpson, and Spiller. Their process is kept secret, but the following method is given by Girard and De Laire:—1000 kilos. of the crude residue from the manufacture of roseine are dissolved in 12,500 litres of boiling water, to which 85 kilos. of hydrochloric acid have been added. Violaniline remains insoluble. The boiling solution is filtered, and to the filtrate 125 kilos. of hydrochloric acid are added. On cooling, a precipitate (A) is formed, consisting of about 40 to 45 kilos. of hydrochlorate of rosaniline, mixed with a little rosaniline and resinous matters.

The filtrate is treated with 625 kilos. of common salt. The precipitate, 30 to 35 kilos., is a mixture of mauvaniline and salts of rosaniline. Name it A. The mother-liquor, filtered off, is saturated with 83 kilos. of soda-ash, containing 58.64 per cent of actual soda. The product, B, 205 to 210 kilos., consists almost entirely of salts of rosaniline, and a very small quantity of salts of chrysotoluidine.

To the filtrate 37 kilos. 500 grms. of soda-ash are added, when a precipitate is formed, 37 to 40 kilos., consisting of chry sotoluidine, with a small trace of rosaniline: 100 kilos. of this last precipitate are dissolved in 2500 litres of lime-water, containing a little lime in suspension. After boiling, the whole is filtered, and the filtrate collected in a crystallising-vat containing hydrochloric acid. On cooling a salt of rosaniline is obtained, containing a trace of chrysotoluidine, and known as yellow magenta. The insoluble residue contains the yellow colour. To remove the lime it is heated in a vessel of enamelled castiron, along with a very little water and hydrochloric acid, just sufficient to saturate the lime. The chrysotoluidine melts, floats on the surface, and is removed with a skimmer and washed a time or two in a little cold water. To remove the last traces of rosaniline 100 kilos. of the skimmings are dissolved in 2000 litres of boiling water, with 100 kilos. of hydrochloric acid. When the solution is made 10 kilos. of zinc are added, and the whole is kept at the boil for eight hours. It is cooled, filtered, and precipitated with 20 kilos. of common salt, the acid being almost entirelly neutralised by the addition of

carbonate of soda. The yield is 80 kilos. of amorphous chrysotoluidine. This is anew dissolved in 2000 litres of boiling water slightly acidulated, the solution is filtered, and precipitated with 50 kilos. of caustic soda at 12° B. The precipitate is collected, washed with cold water, and dried. It is treated with 8 kilos. of sulphuric acid, then with 200 litres of hot water, and kept at a boil for two hours. The solution, when cooled, is precipitated with great care by carbonate of soda, yielding 20 kilos. of a yellowish-maroon matter. The filtrate, containing chrysotoluidine nearly pure, is precipitated with common salt, and yields about 25 kilos. These two substances are then pressed separately, and each is treated with the amount of sulphuric acid required to form a sulphate: 100 kilos of the original crude matter, "C," yield 20 kilos of the yellow-maroon matter, suitable for dyeing skins, and 25 kilos of chrysotoluidine. The formula originally assigned to chrysaniline by Hofmann, who discovered it among the residues of the manufacture of roseine, was C₂₀H₁₇N₃, corresponding to the percentage composition—

				0
C	 	 	 	80.26
Н	 	 	 	5.68
N	 	 	 	14.04

Girard and Chapoteaut discovered chrysotoluidine when studying the action of dehydrogenating bodies upon crystalline toluidine. Its formula is C₂₁H₂₁N₃; and its composition—

C	 	 	 	80.00
Η	 	 	 	6.66
N	 	 	 	13.33

The two bases are isomeric, if not identical. Chrysotoluidine forms well-defined salts with the acids.

Scheurer-Kestner obtained a yellow by dissolving mauveine in hydrochloric acid, and adding tin to the liquid. When all is dissolved common salt is added, by which a yellow matter is thrown down resembling chromate of lead. This matter, collected, drained, and pressed, is exhausted with alcohol, in order to separate the colour from the compound of tin. It dyes wool and silk of a yellowish orange.

Aniline Orange.

In the mother-liquors obtained in the purification of magenta made by the nitrate of mercury process there is found an orange colouring matter, which is separated by precipitating the accompanying substances with common salt. The orange remains in the solution, and is obtained pure by evaporating and washing the residue. It is readily soluble in alcohol, sparingly in hot water, and scarcely soluble in cold water. It dyes silk and wool a beautiful goldenyellow.

Zinaline, $C_{20}H_{19}N_2O_3$, was discovered by Vogel on treating a solution of rosaniline with gaseous nitrous acid. It is insoluble in cold and sparingly soluble in hot water. In alcohol, ether, and chloroform it dissolves readily. It is soluble in acids with a yellow, and in alkaline liquids with a blue colour. It dyes silk and wool a yellow-orange, which can be shaded into red by means of ammonia.

ANILINE GREYS.

Castelhaz prepares an aniline grey by dissolving 10 kilos. of mauveine paste in 11 kilos. of concentrated sulphuric acid, at 66° B. When it is completely

dissolved 6 kilos. of aldehyde are added, and the mixture is allowed to stand for four or five hours. At the expiration of this time it is poured into water. The grey colouring matter dissolves, and the solution, previously filtered, is precipitated with common salt. These solutions and precipitations are repeated until the product is sufficiently pure. This preparation dyes a fine grey upon linen and cotton, but its price is hitherto very high.

Carvis and Thirault prepare a grey (mureine) by dissolving bichromate of potassa and a salt of iron in dilute sulphuric acid, and allowing the mixture to

react upon a bi-salt of aniline, preferably the hydrochlorate.

By varying the respective proportions of the bichromate, of the iron salt, and of the salt of aniline, or by employing other acid salts of the latter, greys may be obtained of a reddish or bluish tone, all which, according to the patentees, are soluble in boiling water, and resist acids and soap better than greys produced by other methods.

ANILINE BLACK.

This differs remarkably from the rest of the aniline colours. It is not a definite chemical compound, but a mixture of at least two distinct colours,—the one an intense blue, bordering upon black, and the other a very deep brown. It is produced by the action of powerful oxidising agents upon a mixture of aniline and toluidine.

This colour is completely insoluble in water, alcohol, ether, benzol, boiling soap-lyes, acids, and alkalies. It has a full, rich, velvety shade, which is turned to a green by acids and restored to its original shade by alkalies. Dilute bichromate of potash increases the intensity of the shade, but, if concentrated, turns it to a reddish hue. Chlorine and the alkaline hypochlorites destroy it in course of time. But if the action has not been sufficiently prolonged for the total destruction of the black, but has merely turned it to a garnet-red shade, the original black gradually returns on exposure to the air, and finally regains its former intensity.

Aniline black has a more powerful affinity for vegetable than for animal fibres. Whether all the various processes for the preparation of aniline black yield products chemically identical is open to question. That it cannot, as maintained by some authorities, consist of mere mixtures of ordinary aniline colours, is proved both by its feebler affinity for wool and silk, and by its insolubility in the usual solvents. Some aniline blacks resist more or less the action of light and of chemical reagents, whilst others turn green more or less readily in contact with air containing acid or sulphurous fumes. The more intense an aniline black, the better it resists these agencies. A black developed in presence of excess of aniline is always more stable than one equally concentrated developed in presence of an excess of acid. Hence the latter class of blacks are unsafe. The tissue is weakened, the black obtained easily turns green, and will not bear bleaching liquor. If the gas used in a warehouse where goods dyed or printed an aniline black are stored should contain a little sulphur, the folds of all the pieces may be turned greenish by the sulphurous acid. When a colour is formed containing excess of base the black will be less likely to turn green, and is better able to bear the action of bleaching liquor. In order that such a black may satisfy all practical conditions, it must be developed with sufficient rapidity to avoid the volatilisation

of the aniline, an object easily attained by using chlorate of aniline instead of chlorate of potash.

Aniline black may be considered as the result of two totally different reactions:—(1). Decomposition of the chlorate of aniline. (2). Oxidation of the aniline salt which is mixed up with the chlorated salt. By the decomposition of the chlorate of aniline, chlorinated products of aniline arise. Many degrees of substitution may be thus formed which would explain the difference of the results. Besides these chlorinated products, which form only a portion of the aniline black, another product is formed, the result of the oxidation of the aniline salt.

Aniline black, commonly so called, consists of two blacks: the one formed by the chlorinated substitutions of aniline is very stable, and resists almost all chemical reagents. Its tone, however, is not so fine as that produced by the admixture of the second product, formed by the oxidation of the aniline salt. This second has an intense violet-blue colour, which when sufficiently concentrated is black. It is much less stable than the other, as it turns green with a trace of free acid, though it resists soaping. The two blacks, the brown and the blue shade combined, form the ordinary aniline black.

The earliest aniline black was printed on calico by the late Mr. John Lightfoot, of Broad Oak Print-Works, Accrington, as early as July, 1860. His colour mixture was—

The colour was printed with madder-pink ground, aged two nights; then the black and pink passed through "Higgins's" alkaline arseniate of soda, mixed with water at 180° F., washed, dunged, dyed in madder, and soaped.

In 1863 this process was patented, with certain modifications. He describes his method thus:—" I take I gallon of water, and dissolve in it 4 ozs. chlorate of potash; to this I add aniline, or any analogous, homologous, or isomeric matter, using by preference aniline, in the proportion of 8 ozs., previously combining it with 8 ozs. of hydrochloric acid at 32° Tw. After stirring well, I add I pint of acetic acid and 8 ozs. measure of perchloride of copper at 88° Tw.; then I add 4 ozs. sal-ammoniac, or an equivalent quantity of other suitable alkaline chloride. I steep the fabric or yarn in this solution, wring out to dry, then I expose the goods in a room at from 60° to 70° F. for two or three days; the goods are now passed through water alone, or a solution containing alkaline or metallic salts, which develope the black much sooner and better. The alkalies and alkaline earths may be used for raising the black, such as caustic soda, potash or ammonia, or lime-water; or the goods may be passed, after printing and dyeing, through a box containing rollers supplied with ammoniacal gas (which I prefer when the black is printed along with steam colours, prior to steaming the goods). When the black is printed along with madder or garancine colours they are aged, at from 60° to 70° F., for three days, and dunged, dyed, washed, and passed through a solution of soap or dilute bleaching-lime, whereby an intense black is produced,"

This process was very successful in block-printing, and came into use to a great extent, especially in Switzerland. For roller-printing it was less adapted, as the acid chloride attacked both the copper rollers and the steel doctors. These defects were partially remedied by using a neutral chloride of aniline, substituting sulphate of copper for the chloride. It is still employed in hand printing and dead-roller work.

Lauth's improvement, patented in England by Hughes, substitutes sulphide of copper for either the chloride or sulphate; his proportions being—16 ozs. salt of aniline, 4 ozs. sulphide of copper, and 4 ozs. chromate of potash.

The sulphide of copper for this purpose is prepared as follows:—Flowers of sulphur are dissolved in caustic soda; the liquor obtained is poured into a solution of sulphate of copper, at the temperature of 75° C. The precipitated copper sulphide is collected upon a filter, and washed.

Keechlin proposes the following formula:-Boil together-

Water	 	 	 to litres.
Starch	 	 	 2 kilos.
Torrefied starch	 	 	 2 ,,
Aniline	 	 	 2 11
Sal-ammoniac	 	 	 4 ,,
Chlorate of potash	 	 	 I kilo.

When it is to be used, add cold-

Sulphide of c	opper	paste	·	 	 I kilo.
Tartaric acid				 	 2 kilos.

The following processes have been found useful in practice:-

Dissolve 300 grms. starch in 2 litres of water, 150 grms. tragacanth in another 2 litres, and 750 grms. of light burnt or torrefied starch in a third 2 litres. Mix together equal weights of these three solutions, and add with heat the $\frac{1}{30}$ th or $\frac{1}{30}$ th part of the weight of this solution of chlorate of potash; let it cool, and add twice as much muriate of aniline as was used of chlorate of potash. If the colour is required for printing, sulphide of copper is added in the same quantity as chlorate of potash.

The appended recipe has done good service:-

5 kilos. of starch solution;

5 ,, light burnt starch solution;

5 .. tragacanth solution :

kilo. chlorate of potash;

I ,, muriate of aniline;

And in the application & kilo. of sulphide of copper.

Spirk boils together I litre of starch-paste (made by dissolving 150 grms. of starch in I litre of water) with I litre of gum solution (7½ grms. of tragacanth to I litre of water) and I litre of gum substitute solution (42 grms. of dextrine to I litre of water. He then adds to the hot mass 90 grms. chlorate of potash and 75 grms. of sal-ammoniac. The mixture is allowed to stand till cold, when 240 grms. of chloride of aniline are dissolved in it, and 75 grms. of sulphide of copper are added just before printing.

For a deep body colour the same author recommends the following:—Boil together, for fifteen minutes, 6 litres of water, 1000 grms. of aniline oil, 625 of chlorate of potash, and 625 of sal-ammoniac. When nearly cold add to it,

with constant stirring, 1000 grms. of tartaric acid dissolved in 1 litre of water. To prepare this colour for printing, boil 1 litre of this mixture filtered, with 135 grms. of starch and the same weight of dextrine, and just before printing add 60 grms. sulphide of copper. Spirk ages for twenty-four to forty-eight hours, at the temperature of 25° to 30° C. The pieces are then passed through an alkaline bath at 75° C., and lastly through a soap bath at 75° to 80° C. If the white grounds appear dull they are passed through weak bleaching-liquor. In the preparation of aniline blacks Hortmann recommends the selection of anilines whose boiling-points lie between 180° to 185° C., and rejects as useless all samples boiling above 192° C., as giving dirty browns or other useless colours.

The best methods of dyeing aniline blacks have also been investigated by Persoz, whose results may be instructive. Some time ago the attempt was made to dye cottons black by passing them through a solution of an aniline salt mixed with bichromate of potash. If the solutions were strong, the colour appeared as soon as the goods left the bath, and speedily became fully developed. A serious difficulty, however, was encountered. If the liquids were dilute no black was produced, and if concentrated the colour was precipitated in the bath. It was attempted to obviate this difficulty by cooling the solutions down to near the freezing-point. This was no improvement, as the chromate of aniline crystallises out, weakening the bath, and causing spots by adhering to the pieces, which were sometimes even charred by the rise of temperature taking place on lifting them out of the solution. Persoz, to overcome these difficulties, causes the pieces to pass through a spray produced by the rapid rotation of brushes in each of the solutions. The same author has examined which aniline salts are practically best suited for dyeing a good black. The tartrate, oxalate, and citrate are either too dear or unfavourable. The experiments were consequently limited to the sulphate, nitrate, and hydrochlorate of aniline. He finds that, for dyeing, the employment of the neutral aniline salts is to be avoided; the binacid salts, especially the bisulphate, give good results, though among the hydrochlorates the teracid salt is preferable. A mixture of bisulphate and terhydrochlorate of aniline gives the best results, the reddish cast of the one being compensated by the blue shade of the other. The solution of bichromate of potash should be used in a concentrated form, not less than 80 grms. per litre.

It makes little difference in the results if the bichromate of potash is applied before or after the aniline salts, or at the same time. The texture may therefore be completely impregnated with the bichromate solution, and immediately after exposed to the spray of the aniline solution. The black appears at first dark green. To develope the colour it is only necessary to wash the goods in water, and then pass through a hot soap bath.

It has been already mentioned that aniline black has a greater affinity for vegetable than for animal blacks. In 1865 Mr. Lightfoot patented a process for applying the aniline black to wool. A solution is prepared with 1 kilo. of dry hypochlorite of lime to 10 litres of water for every kilo. of wool. This bath is composed of—

The temperature of the bath is raised to 38° C., and the wool is worked in it till it has acquired a yellowish colour; it is then withdrawn, washed, and dried. Wool or woollen goods thus prepared are then treated in the ordinary manner, either with Lightfoot's or Lauth's patent black.

Besides the above-described blacks mention must be made of the aniline black pigment of Roberts, Dale, and Co. It is perhaps the best black known for topical printing with albumen colours, as it does not, like logwood blacks,

tarnish the Ginguets, greens, or ultramarine blues.

The Lucas black, otherwise known as "Noir d'Aniline Lucas," or "Petersen's Aniline Black," though much praised at first, has found its level. According to the analysis of Rheineck, it consists of a mixture of hydrochlorate of aniline, and chlorides of copper, iron, and calcium. It finds no favour either with dealers or consumers, and an account of its bad properties has no longer any special technical interest.

The accompanying specimen is printed with the above-mentioned mixture

ANILINE BLACK.

of hydrochlorate of aniline, chlorate of potassa, soda, or ammonia and sulphide of copper added immediately before using. After ageing for two nights the goods are washed off in a hot solution of silicate of soda, washed, soaped, and re-washed.

COLOURED DERIVATIVES OF PHENOL.

Synonyms:—Carbolic Acid, Phenic Acid, Phenic Alcohol, Hydrate of Phenyl,
Phenylated Water.

Phenol is a solid, colourless body, crystallising in long needles, which belong probably to the rhombic system. It has an empyreumatic odour and a burning taste. If touched it attacks the skin, producing white blisters. Its specific gravity is 1.065; it liquefies at 34° to 35° C., and boils between 187° and 188°. Phenol is soluble in alcohol and ether, in concentrated acetic acid, in the tar oils, and in glycerine. It is slightly soluble in water, from which it can be separated by adding saline matter. It is capable of combining with

bases, yet it does not redden litmus, and dissolves alkaline carbonates without expelling the carbonic acid.

Phenol is extracted from the medium and the heavy coal-tar oils by a some what tedious process, which we need not here particularise, but which consists in successive treatment with acid and alkaline liquids. The latter, generally soda, takes up phenol along with the cresylic and phlorylic acids. (See Reimann's "Handbook of Aniline," p. 144). Among its most important derivatives is the rosolic or phenoic acid, or aurine, formed by oxidation, and first obtained by Runge.

Dr. R. Angus Smith prepares rosolic acid by heating in a capsule 2 parts of commercial phenol, with 1 of caustic potash dissolved in a little water, and 5 of peroxide of manganese. A high temperature is required. The resulting mass is dissolved in water, and the alkaline rosolate is decomposed with a

suitable quantity of an acid.

Tscheinitz mixes the heavy tar oils with an excess of hydrate of lime, and leaves the whole in a warm airy place for several months. The red mass thus obtained is powdered and treated with dilute sulphuric acid with the aid of heat. A dense oily scum rises to the surface, and is collected and boiled in water as long as any oily products are volatilised. The fixed residue, when cold, is placed on a filter, washed in water, dried, and treated with alcohol, which dissolves rosolic and brunolic acids. This solution, treated with milk of lime, gives a rose-coloured solution of rosolate of lime, whilst the brown brunolate is chiefly precipitated. Pure rosolic acid is obtained by precipitating the rosolate of lime with acetic acid, and combining it again with lime. This treatment is repeated several times, traces of brunolic acid being eliminated on each occasion. It is finally dissolved in alcohol, and on evaporation remains as a hard vitreous body of an orange colour.

Persoz mixes 3 parts of carbolic acid, 2 of oxalic, and 2 of sulphuric. The carbolic should boil at the constant temperature of 184° C., and the oxalic should be perfectly dry. The whole is heated for some hours to a moderate temperature. During the reaction there is effervescence, the mass thickens, and takes a brownish red colour. The process is at an end when a drop of the mixture, thrown into dilute ammonia, gives an intense red colour. It is then withdrawn from the fire and poured into cold water, which extracts the greater part of the sulphuric acid as well as the sulphophenic acid which has been formed. It is then repeatedly washed with boiling water. On drying it becomes a hard brittle mass, with a green reflection. Rosolic acid gives a variety of fine red shades, which can be easily modified by the aid of reagents. Its unstable character renders the fixation of aurine upon fibres and tissues a matter of some difficulty. The accompanying specimen of "Aurine Orange" was obtained as follows:—Mix well 8 ozs. of aurine solution and 1 gallon of lactarine thickening. The "thickening" is prepared with—

7 pints Water at 80° F.

1 pint Ammonia,

2 lbs. Lactarine.

Stir well until perfectly dissolved. The colour is printed, and steamed for twenty minutes.

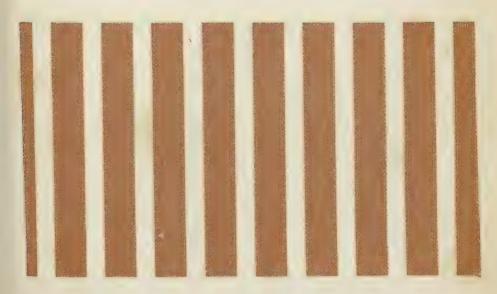
The salts of rosolic acid with the alkaline earths and with lead are now very largely employed in paper staining under the trade-name—very misleading



AURINE ORANGE.

—of Turkey red. It retains, however, its importance as the raw material for the preparation of peonine, or coralline.

This colouring matter was discovered by the younger Persoz, in 1859. To prepare it we introduce into a strong iron vessel, capable of being closed by means of screws, I part of rosolic acid and about 3 of commercial ammonia. The vessel is heated in an oil-bath for three hours to a temperature not exceeding 150°. When cool, the contents of the vessel appear as a thick liquid with a golden crimson reflection. The colouring matter is precipitated from this liquid by the addition of hydrochloric acid. If well prepared, peonine is almost insoluble in water, but very soluble in alcohol, to which it communicates a red colour. Its alkaline solutions gradually take a brown colour on exposure to the air.



CORALLINE YELLOW.

In dyeing with coralline the bath is prepared as follows:—The colour is dissolved in alcohol, a little soda added, and the alkaline liquid poured into a large quantity of water. By a slight addition of tartaric acid the colour is set at liberty without being precipitated. In this bath shades are obtained intermediate between those of cochineal and magenta. Cotton requires to be previously mordanted with tin-salt and sumac or gall-nuts. The goods are then entered into the colour-bath, which should be lukewarm, and are worked for ninety minutes. For a full shade 500 grammes of coralline are consumed per piece. The shade obtained resists steaming and washing, but is quickly affected by soap, alkalies, and light. By a momentary exposure to ammonia it may be modified to a carmine, but this colour is exceedingly unstable.

Coralline thrown down from its solution in acetic acid by the addition of water, and dried at a temperature below its point of fusion, is a fine red powder, which can be printed as a pigment colour by means of albumen.

Yellow coralline is a modification of the above colour; the exact mode of the preparation has not been made public. It yields upon wool very fine orange shades, which are thus obtained:—2½ kilos. of yellow coralline are dissolved in 10 litres of caustic soda at 10° B. at the temperature of 60° C. It is poured into 100 litres of water, heated again, and when completely dissolved 1 litre of bichloride of tin at 55° B. is added, previously diluted with 5 litres of water. On filtering we obtain 20 litres of a bright orange lake. 10 litres of this without previous washing are mixed with 2 kilos. of powdered gum and 350 grms. of oxalic acid. The mass is heated till the gum and acid are dissolved, strained, and printed on wool. After twelve hours it is steamed for forty minutes.

The accompanying specimen of coralline yellow is produced by the following process. The colour is dissolved in dilute ammonia to the strength of 32° Tw. One measure of this solution is mixed with 4 measures of starch paste, containing 14 lbs. per gallon, printed, dried, and steamed for one hour.

The following formula gives a good red upon delaines, resembling Turkey red:—

Red coralline 80 grms.

Dissolve in a hot mixture of γ_0 litre of glycerine and $\frac{1}{4}$ litre of water. In a separate vessel 140 grms, of calcined magnesia are stirred up in $\frac{1}{4}$ litre of water. The whole is then mixed together with $\frac{3}{4}$ litre of solution of gum, containing 500 grms, per litre.

Another derivative of phenol is picric acid, otherwise known as trinitrated phenic acid, carbazotic acid, nitrophenisic acid, nitropicric acid, &c. It is produced by the action of nitric acid upon indigo, silk, aloes, the resin of Xanthorrhea hastilis, and especially phenol. The present mode of manufacture is to pass, in small quantities at a time, a stream of nitric acid into pure carbolic acid, or into a previously formed mixture of carbolic and sulphuric acids, or better still by attacking the crystalline sulpho-carbolate of soda with nitric acid. Picric acid forms small brilliant yellow crystals, of an intensely bitter taste, and moderately soluble in water. It dissolves in sulphuric and nitric acids without change, and is re-precipitated on the addition of water. Its tinctorial power is enormous, and its affinity for animal fibres is very great, but upon vegetable fibres and tissues it can only be fixed by the aid of animal mordants. With bases picric acid forms a series of well-defined salts,

which are in general soluble, crystallisable, yellow, and which if heated, especially in a closed vessel, explode with great violence. The picrate of soda is sometimes sold to dyers under the name of aniline-yellow, but its use requires care. Picric acid dyes upon silk and wool shades varying in depth from a straw-yellow to a maize. Wool is easily dyed either hot or cold, and is often previously mordanted with alum and tartar to render the colour faster. Picric acid is also used along with extract of indigo, and with Prussian blue, for producing greens, and in modifying the tone of the aniline greens.

The intensity and purity of a sample of picric acid may be known by dyeing known weights of wool or silk with a given quantity of the dye, and comparing the shades produced with those furnished by a standard sample. It is frequently adulterated with a variety of articles, such as sulphate of soda, borax, oxalic acid, alum. These impurities are easily detected by dissolving the sample in benzol, warming the tube gently by plunging it into lukewarm water. The impurities remain insoluble.

Picramic acid may be prepared by dissolving I part of picric acid and 7 parts of protosulphate of iron in hot water, and adding a boiling solution of caustic baryta. A deep red liquid is obtained, containing the picramate of baryta. Girard saturates with ammonia picric acid dissolved in alcohol, and treats the solution with an excess of sulphuretted hydrogen. The liquid takes a dark red colour, and deposits a mass of deep red crystals, the picramate of ammonia. This salt is dissolved in boiling water, mixed with an excess of acetic acid, and allowed to cool. Picramic acid crystallises after a time in the form of tables or needles of a brilliant garnet red. It is easily soluble in alcohol and ether, sparingly in water, even when hot. Both picramic acid and the soluble picramates are true dyes, capable of fixing themselves upon animal fibres, but they have not yet found their way into commerce.

Isopurpuric Acid.

(Picric Red, Picrocyanic Acid, Homorceine, Soluble Garnet.)

This colour is prepared by dissolving 2 parts cyanide of potassium in 4 parts of water at 60°. A solution of 1 part of picric acid in 9 parts of boiling water is then gradually added with constant stirring. On cooling there is formed a crystalline mass. This is thrown on a table, pressed, stirred up in a little water, filtered anew, and washed with cold water. The residue is purified by re-solution in boiling water, and re-crystallisation. The potash salt thus obtained is dissolved in a small quantity of hot water, and a solution of sal-ammoniac is added. It is deposited in wedge-like crystals, of a reddish brown colour, with metallic green reflection. The isopurpurate of ammonia was at one time considered identical with the purpurate of ammonia (murexide). A careful comparison of the shades produced by these two dyes under identical conditions proves a decided difference. Isopurpurate of ammonia has been prepared on a commercial scale by Messrs. Roberts and Dale, of Manchester, and yields beautiful and peculiar reddish purples on wool, leather, and silk. Its use, however, is still very limited. When dry the isopurpurates explode with a fearful violence on the least shock. Hence they should be preserved in a paste with water and a little glycerine, which prevents drying up.

Rothine, or Phenicienne.

(Not to be confounded with phoenicine). This colour was discovered by Roth in 1863, and has been prepared on a large scale at Mulhouse. It is obtained by pouring nitrosulphuric acid upon carbolic acid. The proportions are to to 12 parts of the former to 1 of the latter. A small part of the nitro-sulphuric acid is added at first, and the rest is added in successive portions as the reaction ceases, until no more orange vapours are given off on the last addition of acid. The whole is then thrown into a large quantity of water. An abundant brown precipitate is immediately formed, which, when collected, washed, and dried, is phenicienne. The washing is a tedious process, lasting several days. The colour is sparingly soluble in cold, and completely insoluble in hot, water; very soluble in ether, alcohol, and acetic acid, especially if a little tartaric acid has been added previously. Phenicienne is also readily soluble in alkaline liquids. It furnishes a great variety of solid shades, according to the mordants employed. It resists sunlight, and even chloride of lime. The shades which it yields surpass in purity and brightness all similar colours obtained with the woods and orchil. It has certain analogies with catechu, and its shades are heightened in a similar manner by metallic salts capable of exerting an oxidising action.

With silk and wool it is a substantive colour, the shades produced varying from a deep garnet to a deep chamois, according to the concentration of the colour-bath and the oxidising agents employed.

Cotton goods are previously mordanted with tannin and stannate of soda. Alkalies give the colour a blue cast, but the dye is then attacked by soap.

Phenicienne does not give satisfactory results in printing, even on wool and silk; the process of steaming destroying its brilliancy.

Vesuvine.

This is a colour discovered by Knorp, of Stuttgardt. Its nature and preparation have not been closely described, but it is probably identical with the dye patened by Messrs. Roberts and Dale, as "Manchester Brown," and produced by the action of alkaline nitrites on phenylen-diamine. Vesuvine dyes orange and light brown shades. For use it is dissolved in tepid water and filtered. This solution dyes wool and silk at the heat of 87° or 88° C. The addition of hyposulphite of soda to the extent of one-tenth the weight of the colour is advantageous as regards wool. A variety of brilliant shades can be produced by the addition of a solution of chloride of tin neutralised with ammonia. Cotton tissues are first prepared with sumac; then worked in weak stannate of soda, wrung out, passed through water slightly acidulated with sulphuric acid, rinsed in cold water, and worked in the dye-bath.

NAPHTHALIN COLOURS.

Naphthalin was discovered in coal-tar in 1820, and was first investigated by Faraday in 1826. Its percentage composition is—

Carbon	 	 	 	 93.7
Hydrogen	 	 	 	 6.3
				00.0

and its formula is C10H8.

When pure it is a colourless solid of peculiar smell and taste. Its specific gravity is 1.153. It melts at 79° C., and boils at 220° C. It is insoluble in cold water, sparingly soluble in boiling water, but dissolves readily in alcohol, ether, the fatty and essential oils, and in acetic acid. It dissolves easily sulphur, phosphorus, indigo, iodine, the iodides of lead and mercury, the sulphides of arsenic, tin, and antimony, and arsenious acid.

The derivatives of naphthalen are almost innumerable, and many colouring matters are produced by its reactions, few of which, however, have found their way into commerce. Among the most important of its products we mention naphthylamine, which yields a red and a violet dye. This substance is composed of—

Carbon	 	 	 	 83.91
Hydrogen	 	 	 	 7.55
Nitrogen	 	 	 	 8.54
				100,00

and has received the formula, C10H9N.

It is a solid body, crystallising in colourless needles, of offensive odour, and burning taste. It fuses at 50°, and sublimes at 300°. In water it is almost insoluble, but it dissolves readily in alcohol and ether. It combines with the acids to form salts, which, on exposure to the air or to oxidising agents, take a red or violet colour.

Naphthylamine Violets.

One kind of violet resulting from the above-mentioned action of oxidising agents upon the salts of naphthylamine was discovered by Piria, in 1851. Its constitution is unknown. The other kind is produced by the action of dehydrogenisers upon naphthylamine at the temperature of 200°. Their production generally accompanies that of naphthylamine red. Neither of these violets has yet been prepared on a large scale.

Naphthylen Diamine Violets.

These colours result from the action of reducing agents upon binitro naphthalin. Troost prepares them by treating binitro-naphthalin with sulphides, cyanides, and sulpho-cyanides in presence of an alkali, which must not be allowed to act before the reducing agent. The violet bodies produced dissolve in alkalies, alkaline carbonates, and alcohol, from which they are precipitated unchanged by dilute acids.

Roussin treats binitro-naphthalin with proto-salts of tin dissolved in caustic alkali. If the heat of the water-bath be applied the reaction is complete when the temperature reaches 80°. The mixture is then thrown upon a filter, and washed as long as anything is dissolved. A violet-blue powder remains on the filter, easily soluble in alcohol and wood-spirit, and capable of dyeing fast shades.

Naphthalin Yellow.

Martius has patented the manufacture of a yellow dye by adding an alkaline nitrite to an acid solution of the hydrochlorate of naphthylamine. When a little of the liquid thus obtained gives a cherry-red with alkalies, it is mixed with a large quantity of nitric acid and boiled. The resulting acid is

of a pale yellow colour, and forms beautiful crystals with the alkalies and alkaline earths. The lime-salt is largely manufactured by Messrs. Roberts and Dale, and is known under the trade-names of Manchester Yellow and Jaune d'Or. Its tinctorial power is still greater than that of picric acid, to which it is in many respects analogous. Indeed, it may be regarded as a picric acid, in which the radical phenyl is replaced by naphthyl. It produces upon silk, wool, and leather bright shades of a true gold colour, without the greenish cast of picric acid. These colours bear the steaming process, which is not the case with those obtained with picric acid.

It was at one time thought that alizarin had been obtained artificially from naphthalin. This opinion proved to be unfounded, but artificial alizarin, as we shall see below, is produced by another of the coal-tar products.

Many of the coloured reactions of naphthalin and its derivatives invite further research.

ANTHRACEN COLOURS. Artificial Alizarin.

Anthracen is a solid body, existing in the heavy oils of coal-tar. It is met with in the last portions, which distil after napthalin. It is not equally plentiful in all tars, but is chiefly found in those which are rich in benzol and naphthalin, poor in toluen. According to Berthelot, toluen at a red heat yields anthracen as the principal product of its decomposition. existence of anthracen in coal-tars is due to the previous destruction of a part of the toluen which they contain, the rarity of the one substance must correspond with the abundance of the other. On the large scale anthracen is prepared as follows:—If coal-tar is distilled in the usual manner it yields on the average per ton 13 to 14 litres of ammoniacal gas-liquor; 29 to 30 of very light oils, containing benzol; go to 100 of light oils, containing a little benzol. If the distillation is continued, 300 to 312 litres of heavy oils are collected, and the residue is merely hard pitch. The heavy oils consist of naphthalin, phenol, cresol, and similar products, and contain besides more or less anthracen. The last-mentioned body passes over towards the end of the process. When the fatty matter which distils over shows a yellowish green colour, and congeals to a pasty consistence on cooling, it is collected separately. It contains about 20 per cent of anthracen, and is used as the chief material for its preparation. The mass is placed in a centrifugal machine to expel the oil as far as possible. The residue, which still contains much oil, is heated to about 40° C., and introduced into a powerful hydraulic press, which should be provided with plates capable of being heated like an oil-press. The residue, after pressing, contains about 60 per cent of pure anthracen. In this state it is a greenish, tolerably dry mass. It is then treated with light tar-oil or with petroleum-naphtha, boiled and allowed to cool, or extracted by percolation. The light oil dissolves the residue of naphthalin and the heavy oil, whilst pure anthracen moistened with naphtha remains behind. This pure anthracen is again extracted in the centrifugal, placed in a boiler, and heated to the melting-point, when the residues of the light oils distil over. There remains a greenish-white, paraffin-like mass of fine crystalline fracture, containing 05 per cent of pure anthracen, and melting at 205° to 208° C. By sublimation pure anthracen is obtained in small lamellar crystals, which melt at from 212° to 215°. A trustworthy method for determining the amount of pure anthracen, either in commercial anthracen or in crude green grease is the following:—The melting-point of the sample in question is first determined. 5 to ro grms. are sufficient for the operation. It is put between thick folds of blotting paper, and placed under a press, between plates which have been previously warmed. The anthracen remaining upon the paper after pressure is weighed. The residue, after it has been boiled with a certain quantity of alcohol, filtered, washed with cold alcohol, and dried, is weighed as pure anthracen. It is now advisable to determine the melting-point of the purified product, which will generally be 210° C.

The methods by which anthracen may be extracted from the less volatile oils and from the residual pitch need not be here described. The products of anthracen are very numerous, but the only one which concerns us is artificial alizarin. Its preparation, according to the earliest patent of Graebe and Liebermann, is as follows:—Purified anthracen $(C_{I4}H_{I0})$ is converted into anthrachinon, $C_{I4}H_8O_2$, either—

- By treating 1 part of anthracen with 2 parts of bichromate of potash and sulphuric acid, with or without acetic acid.
- By oxidising anthracen with bichromate of potash, both dissolved in acetic acid.
- By oxidising anthracen with nitric acid of medium concentration, and simultaneous application of concentrated acetic acid.

The anthrachinon thus obtained is converted into $C_{14}H_6Br_2O_2$ by heating 1 equivalent of anthrachinon and 4 equivalents of bromine in closed vessels, for several hours, to the temperature of 80° to 130° C. The bibromanthrachinon is then heated in closed vessels, with concentrated soda or potash-lye, to 180° to 260° C., in order to replace the bromine with peroxide of hydrogen. The mixture slowly assumes first a blue and then a violet colour, which gradually becomes more intense. When the depth of colour no longer increases the mass is allowed to cool, dissolved in water, filtered, and supersaturated with sulphuric or hydrochloric acid, when alizarin separates out in yellow flakes, which are filtered and purified by washing with water.

The third patent of the same chemists (dated November 3, 1869, and January 18, 1870) directs the preparation of artificial alizarin as follows:—

One part of anthrachinon is mixed with about 3 parts of concentrated sulphuric acid (sp. gr. 1.848), and the mixture is heated in a suitable vessel till a portion poured into water dissolves completely, and leaves only traces of unchanged anthrachinon. It is then allowed to cool, and diluted with water. In order to remove the excess of sulphuric acid it is accurately saturated with chalk. Sulphate of lime is thrown down, and is removed by filtration and powerful pressure, whilst anthrachino-bisulphate of lime remains in solution. As this salt is insoluble in cold water, this operation should be conducted at a boiling heat. The hot solution is mixed with a solution of carbonate of soda, likewise hot, till the reaction is alkaline. The mixture is boiled for some time, till the carbonate of lime is deposited in a heavy granular state. The solution of anthrachino-bisulphate of soda is separated by decantation and filtration, and evaporated to dryness. To I part of the dry salt, 2 or 3 parts of solid soda and a little water are added. The mixture is then heated in iron vessels to 180° to 260° C., till the fused mass has an intense violet colour, and a portion dissolved in water and mixed with dilute sulphuric acid gives a copious

brownish-yellow deposit. When this point is reached the mass is allowed to cool, dissolved in hot water, the deep blue violet liquid decanted or filtered from the undissolved residue, and the clear filtrate mixed with sulphuric or hydrochloric acid. Sulphurous and carbonic acids are evolved, whilst alizarin is deposited in dense brownish-yellow flakes. These, when cold, are collected on a filter, and perfectly washed with cold water. The alizarin can serve for all purposes to which the preparations of madder were formerly applied.

Anthrachinon-bisulphuric acid is prepared from anthracen as follows:-I part of anthracen is heated in a suitable vessel with 4 parts of concentrated sulphuric acid, at first for 3 hours to 100°, and afterwards for another hour to 150°. The mass, when cold, is mixed with three times its weight of water. If unchanged anthracen is deposited, it is collected, washed, dried, and set aside for a future operation. The strongly acid dark coloured solution contains anthracen-bisulphuric acid and much free sulphuric acid. It is heated to boiling, and peroxide of manganese in powder is added to thrice the weight of the anthracen employed. The boiling is kept up till the anthracenbisulphuric acid is converted into anthrachino-bisulphuric acid. The mixture should be evaporated to dryness, and the heat continued for some time. The mass is now dissolved in boiling water, and dilute milk of lime is added, till the liquid has an alkaline reaction. Insoluble protoxide of manganese is deposited along with sulphate of lime, whilst anthrachino-bisulphate of lime remains in solution. All insoluble matter is removed by filtration and pressing, and the residual solution of anthrachino-bisulphate of lime is decomposed by means of carbonate of soda. The solution is evaporated to dryness, and converted into alizarin by treatment with acids.

Dale and Schorlemmer have patented a still simpler process:—I part of anthracen is boiled for some time with 4 to 10 parts of strong sulphuric acid It is then diluted with water, and the solution neutralised with carbonate of lime, baryta, soda, and potash. The sulphates are then removed by filtration or crystallisation. The resulting solution is heated to 180° to 260° C., along with caustic soda, to which a quantity of saltpetre or chlorate of potash, equal in weight to the anthracen originally employed, has been added, until the deep blue-violet colour is developed. The alizarin is then thrown down with acids in the usual manner.

The alizarin of commerce generally forms a thin paste, containing about 15 per cent of solid matters, alizarin, anthrachinon, and oxyanthrachinon. To prepare from this paste pure alizarin it may be dissolved in dilute caustic soda and filtered. The filtrate is mixed with chloride of barium, boiled, filtered, and the precipitate is well washed with water, then suspended in water, and decomposed with hydrochloric acid. The orange-coloured precipitate is filtered, washed, dried, and sublimed, when pure alizarin is obtained.

The identity of artificial and natural alizarin was for a time doubted, in consequence of experiments made with impure products. Certain chemists found that tissues dyed with artificial alizarin lost a considerable amount of colour on treatment with soda-lye. This result was probably due to the presence of tinctorial matters other than alizarin. The artificial alizarin paste of Gessert and of Lucius has, according to Bolley, ten to twelve times the tinctorial power of Italian garancin. For the properties of alizarin the

reader is referred to the section on the madder colours, where also will be found a specimen dyed with artificial alizarin for comparison with a Turkey red.

The following recipes for printing with artificial alizarin will be found useful:—

Reds.

5 lbs alizarin paste (10 per cent);

16 lbs. thickening;

1 lb. acetate of alumina, at 15° Tw.;

1 lb. acetate of lime, at 25° Tw.

Pinks.

The same, diluted with 2 or 3 parts of thickening.

For double printing, when deep red is printed on first, the goods must be steamed one hour before the second printing takes place. After the second printing the goods are again steamed for one hour and aged for twenty-four hours; they are then passed through one of the following baths, at from 120° to 140° F., remaining in the bath not longer than 1 to 1½ minutes:—

250 gals. water;

60 lbs. chalk;

3 lbs. tin crystals.

Or 250 gals. water;

40 lbs. chalk;

10 lbs. arseniate of soda.

The goods are then washed and cleared as follows:—Take for 10 pieces of 50 yards each—

1st soaping, at 120° F., 3 lbs. soap; \(\frac{1}{2}\) lb. tin crystals.

at 160° F., 3 lbs. soap.

3rd ,, at 175° F., 3 lbs. soap.

Wash between each soaping.

Red for Mosaics.

8 lbs. alizarin paste (10 per cent);

10 quarts thickening;

9½ ozs. nitrate of alumina, at 23° Tw. ;

19 ozs. acetate of alumina, at 15° Tw.

13 ozs. acetate of lime, at 25° Tw.

Or 10 lbs. alizarin paste (10 per cent)

to quarts thickening;

13 ozs. nitrate of alumina, at 23° Tw.

19 ozs. acetate of alumina, at 15° Tw.

16 ozs. acetate of lime, at 25° Tw.

Another Red without Oil.

81 lbs. alizarin paste (10 per cent);

9} lbs. acetic acid, at 12° Tw.;

31 lbs, wheat flour;

5 pints water.

Boil well, and stir till cold; then add-

1 lb. acetate of lime, at 29° Tw.; 2 lbs. nitrate of alumina, at 23° Tw.; 3 lbs. hyposulphite of lime, at 13° Tw.

Purple.

3 lbs. alizarin paste (10 per cent); 10 quarts purple thickening; 6 ozs. pyrolignite of lime, at 18° Tw.; 12 ozs. acetate of lime, at 25° Tw.

The printed goods are steamed for an hour or two, and then aged for twenty-four to thirty-six hours. They are then padded in the chalk and arseniate of soda bath; after which they are washed and soaped in a single soap-bath without tin-crystals, and if needful cleared in a weak solution of bleaching-powder.

Thickening for Reds.

12 lbs. wheat starch;
40 quarts water;
4 quarts acetic acid, at 9° Tw.;
1½ lbs. gum tragacanth;
2 lbs. olive oil;

Boil well together, and stir till cold.

Thickening for Purple.

ro lbs. starch;
27 quarts water;
3 quarts acetic acid;
1½ lbs. gum tragacanth;
2 lbs. olive oil.

Boil well together, and stir till cold.

The mordants in the above recipes are prepared as follows:-

Acetate of Alumina.

Stir 30 lbs. hydrate of alumina into 6 quarts of acetic acid, warm, filter, and reduce to the specific gravity required.

The hydrate of alumina is prepared by dissolving 72 lbs. alum in 100 gals. water, and 62 lbs. soda in 100 gals. water. The two solutions are mixed, the precipitate is washed eight times by decantation, collected on a filter, and pressed. It must be dissolved on the filter before it gets dry.

Nitrate of Alumina.

2 lbs. nitrate of lead;

2 lbs. alum;

2 quarts water.

Dissolve and filter off the liquid from the precipitate, and dilute to proper standard.

The reds are turned more yellow by nitrate than by acetate of alumina, and when the former is used more acetate of lime is taken in addition.

Acetate of Lime.

A solution of acetate of lime at 25° Tw. contains 25 per cent of acetate of lime: generally 10th of the weight of alizarin paste is required; but with a fresh quality of alizarin it is safer to ascertain, on a small scale, the amount needed.

Brown.

- 131 lbs. alizarin paste (15 per cent);
- quarts thickening;
- 2 lbs. nitrate alumina, at 20° Tw.;
- 15 ozs. acetate alumina, at 19° Tw.;
- 15 ozs. red prussiate of potash, dissolved in water;
 - I lb. I oz. acetate of lime, at 29° Tw.

To obtain a yellower shade, for every quart of mixed colour, r oz. of bark liquor, at 30° Tw., may be added.

Old spoiled red colours may be advantageously used for browns by adding per quart \ oz. to 1 oz. of red prussiate, dissolved in water.

CHAPTER IV.

COLOURING MATTERS OF VEGETABLE AND ANIMAL ORIGIN.

MADDER AND OTHER RUBIACEÆ.

"OF all the dye-materials in general use none exceeds in importance madder, which has become the basis of almost all our dyes." These words, written in 1828 by Daniel Kæchlin-Schouch, are scarcely out of date even at the present day. Madder owes its importance to the beauty and fastness of the tints it yields, and to the fact that by a simple variation of the mordants used it produces red, rose-pink, black, violet, lilac, and puce colours. Though alizarin, the chief colouring matter of madder, is now produced artificially in large quantities, madder will long remain in request, especially for woollen dyeing. 1000 tons of coal should theoretically yield 1 ton of alizarin; in practice the amount obtained does not exceed one-half of this estimate. The future of artificial alizarin depends on an increased supply of anthracen.

Madder, garance (Fr.), meekrapp (Dutch), krapp (Germ.), robbia (Ital.), is the ground root of a plant known to botanists as Rubia tinctorum. It is originally a native of Central Asia and the table-lands of the Caucasus. This root has been cultivated from a remote antiquity, -so remote, indeed, that it is very difficult to say where its true habitat may be. Its cultivation in the neighbourhood of Smyrna, Adrianople, the Isle of Cyprus, and some parts of the present kingdom of Greece, is mentioned by ancient historians. Dioscorides and Pliny state that madder was used by the Egyptians, Persians, and Indians. The ancient Greeks and Romans were acquainted with this plant under the names of Erythrodanon and Rubia. About the time of the Crusades the cultivation of madder was re-introduced into the more western parts of Europe, especially into Italy, and perhaps into France. In some parts of Spain it was grown by those enterprising agriculturists, the Moors, and towards the middle of the sixteenth century it found its way into that portion of the Netherlands known as Zealand. Charles Gaint caused it to be cultivated in Alsace, and Colbert introduced it into the Comtat d'Avignon in 1666. In the city of Avignon the general tradition is that a certain Armenian, named Joseph Althen, a native of Yulfa, a suburb of Ispahan, introduced the culture of madder into the Comtat and the neighbouring principality of Orange, about the years 1762 to 1774. A statue has been erected at Avignon in his honour, and was inaugurated on the day that his only daughter died in an hospital. The cultivation of madder in Alsace (late Départements du Haut et Bas Rhin) is locally attributed to M. Franke, of Haguenau (1760). In our days madder is cultivated, to a greater or less extent, in Italy, Roumania and other parts of Turkey, the States of Barbary (Tunis, Morocco), various parts of Germany and of Spain; the provinces of Zealand, North Brabant, and Limburg, in the Netherlands; some parts of Belgium, the Caucasus, the Levant, North and South America, and Algeria. Its cultivation has never been carried on to any extent in the United Kingdom.

The plant is an herbaceous perennial belonging to the natural order Rubiaceæ, or, on the old Linnean system, to the Tetrandria Monogynia. There are three varieties of this plant in cultivation,-Rubia tinctorum, R. cordifolia, and R. peregrina. The stems of the plant are squarish. The blossom is yellow, and it is succeeded by a small berry containing the seeds. The valuable portion of the plant is the root, which is long in proportion to its thickness, and, except in some Levant roots, not exceeding a goose-quill in diameter. This root consists of three distinct portions,—the epidermic cuticle, the cortical fleshy and cellular ring, and the hard internal woody portion of a fibrous structure. According to the researches made by M. E. Keechlin, the following proportions exist between the different portions of the roots, calculated for 100 parts of the fresh material: Fleshy matter, 90'36, equal to 16'94 after drying; ligneous parts, 9.64, after drying 4.68. The root alone contains the colouring matter, and the name "madder"-or its equivalent in foreign tongues-is rather incorrectly applied to the living plant as well as to the dried root, ground or whole, except that in many countries the unground root is called "alizari" or "lizari." In commerce three kinds of madder are chiefly distinguished, viz., Avignon, Alsatian, and Dutch. In addition, we shall briefly mention the madders derived from other countries. The cultivation of the so-called Avignon madder is chiefly confined to certain districts of the Vaucluse which were once marshy, and which, having been drained, stretch from l'Isles to Eutraigues, forming what are locally known as "paluds." This soil is rich in humus, and in carbonate of lime, and is of a very open texture. When dry it is almost white, but becomes brownish when moistened. There is reason to believe that in former ages this part of France was entirely submerged. Schlumberger found, on analysis, the composition of this soil to be-after desiccation at 100° C .-

inter desiccation at 100 C.	Palud	District.		ielding oloured lder.
Carbonate of lime	ī. 93	II. 90	Superior.	Inferior.
Insoluble in hydrochloric acid	6	5	50	90

Trace of oxide of iron. Trace of oxide of iron.

The palud roots are very rich in colouring matter, and exhibit in their centre a deep red colouration. The roots grown in a soil richer in clay exhibit a rather yellow—or, more correctly speaking, rose-pink—colour. As regards the quality of the soil best suited to the cultivation of madder, it is difficult to give a clear description, seeing that the crop succeeds well under widely different conditions of soil, climate, and treatment. Thus there is no point of comparison between the soils just referred to and the soil upon which madder is successfully grown in the province of Zealand. Further, a difference of some 10° of latitude cannot fail to bring about a corresponding variation of climate. Whatever may be the nature of the soils applied to the cultivation of it, it requires careful tillage. The ground is ploughed to the depth of 60 to 80 c.m., and is well manured with rich but well-rotted horse-dung, or farm-yard manure. In the Vaucluse, madder is sown about the month of March, and the young plant

is very carefully tended and kept free from weeds. Experience having shown that the older the root the richer it is in colouring matters, the plant is left in the soil at the very least for eighteen months, but often for a longer time. Care is taken to promote the development of the root by covering the portions above ground with soil, thus preventing its too rapid growth. The plant blooms in July, and the seed is collected in August. The plant is cut down with sickles, the stem and leaves being used as food for cattle. In November, the plant having been in the ground for eighteen months (which is technically called two years) or 28 months (called three years), the root is dug out, an operation which in the Vaucluse is performed by means of a speciallyconstructed plough. The yield of roots at two years of age varies considerably, but on the average amounts to 16,000 kilos. of fresh root per hecare, equal to 4000 kilos, of dried lizari. The price of the air-dried root in this district varies from 65 to 70 francs per 100 kilos., and the department of the Vaucluse produces yearly madder to the value of 25 to 30 millions of francs. The dryness of the air and the heat of the sun suffice for the desiccation of the root so as to fit it for the grinding-mill and for transportation.

The cultivation of madder in the Netherlands is chiefly, though not entirely, confined to those parts of the country which have been reclaimed from the sea, and are commonly termed "polders." The soil is chiefly a rich alluvial clay, and does not contain nearly so much lime as the paluds district of the Vaucluse. It may be advisable here to quote the full analysis, made some years ago by Mulder, of the surface and subsoil of the best Zealand madderclays, of the earth from the palud district, and of the ash of the best Alsace madder-root by Kæchlin, and of Zealand madder-root by Mulder.

SURFACE SOIL,	ZEA	LAN	D, A	IR-D	RIED.	
Sodium chloride						0.013
Potassium silicate						0.484
Sodium silicate						0'314
Sodium carbonate						0.064
Calcium sulphate						0.122
Calcium carbonate						13.028
Potassium carbonate						0,000
Potassium chloride	-			4.0		0'000
Manganic and ferric se	esqu:	ioxid	es			3.387
Alumina						1.218
Phosphoric acid						2.688
Subsoil from	h.e. 131.9	· n &	1 3 5 12	17mm		
Sodium chloride		* *				0.014
Potassium silicate						0.630
Sodium silicate						0.013
Sodium carbonate						0.538
Calcium sulphate						0.248
Calcium carbonate						13.930
Magnesium carbonate						0.69
Potassium carbonate						0.020
Manganic and ferric s	esqu	ioxid	les			2.310
Λlumina						1.302

Phosphoric acid o 500

Residue to make up 100, moisture, silicates, &c., insoluble in hydrochloric acid.

PALUDS EARTH, VAUCLUSE.

					0.132
					0.588
					0.500
					0.226
					87.060
					0.162
					0.131
					0.000
squ	ioxid	es			2°134
					0.720
					1.266
					0.030
	esqui	squioxid	esquioxides	squioxides	squioxides

Ash of Alsace Madder (Kechlin). (Two samples grown in different fields).

		-			,
				I.	11.
Potassa			 	29'35	28.64
Soda			 	15.89	11.67
Lime			 	34.24	29.25
Magnesia			 	3.72	3.68
Peroxide of	iron		 	1.18	3.36
Phosphoric	acid.		 	5.26	4.62
Chloride of	sodiu	m	 	4.71	13.25
Sulphuric a	cid		 	3.68	2.14
Silica			 	1.64	5.36

ASH OF ZEALAND MADDER ROOT.

Potassa	 	 	 25'48
Soda	 	 	 21.01
Lime	 	 	 15.84
Magnesia	 	 	 0.11
Peroxide of iron	 	 	 10.18
Phosphoric acid	 	 	 3.63
Chloride of sodium	 	 	 7.72
Sulphuric acid	 	 	 3°27
Silica	 	 	 10.87

Madder is not grown from seed in Zealand, but shoots are planted in the month of May, and put in well-tilled ground, in rows about 2 feet or more apart. The plot is carefully weeded, and in the month of November following the plants are covered over with earth, dug from between the rows, to preserve them from frost. This treatment serves to increase the roots in length and thickness. The roots are dug out with long narrow-bladed spades.

In Alsace the root is planted in a clay soil not containing much lime. The plants are raised from seed, but the roots in shape resemble those of Zealand,—that is, they form a bunch going 2 or 3 feet down into the soil, and occupying a considerable surface, whilst Avignon madder is a long straight root with small rootlets attached. The madder of commerce is the root ground

down to a powder, but it undergoes some previous operations to fit it for grinding. The root when first dug out is very brittle, and is hence left on the fields for twenty-four hours after being dug up, in order to grow tough. In the Caucasus the root is washed in water, to remove adhering soil,—a process which in Europe has been condemned as injurious without trial, and which might be advantageously tried. After washing it is next placed in pits dug in the ground, similar to those used by farmers for storing potatoes during the winter. In these some brushwood is burned, probably to fill the pit with empyreumatic vapours, whereby the possibility of fermentation and decay of the madder is prevented. The roots are then covered over with soil, and left in the pits for some five or six months. After this lapse of time the madder is found to have lost all its sugar and the other inert vegetable matters it contains. It is next dried in the sun, and after this treatment is known as Marina. Its tinctorial power is greatly enhanced by this process. In Alsace and Zealand the root is dried artificially in kilns. In Zealand peat is generally used as fuel, and in the kilns the smoke and gaseous products of combustion are let pass through and over the roots. In the more improved establishments steam or hot air is employed with advantage. By this drying the root is enabled to keep, and rendered more marketable. A second drying has to be performed to fit it for grinding.

The fresh root contains from 70 to 80 per cent of water. That from Alsace and Zealand, and indeed from any clay soil, is rich in sugar and other substances, which render the drying more difficult. After drying, the root still retains 15 to 19 per cent of water, which can only be got rid of by exposure for twenty-four to thirty-six hours to a temperature of 50° to 60° C.

A higher heat is injurious, and even at this temperature combustion sometimes ensues. After drying, the roots are beaten with thrashing-machines, to remove sand, clay, and rootlets. The latter, along with some of the bark of the roots, are separated by means of sieves, and sold for dyeing. Levantine, Spanish, and Neapolitan roots generally find their way to Avignon, to be there ground up. These contain only 12 to 14 per cent of water, and are easily dried. The alizaris (unground roots) are met with in commerce packed in bags or casks, weighing, for the countries, above o to 10 cwts. The Vaucluse alizaris are packed in coarse canvass bags, and weigh from 13 to 2 cwts. Zealand roots were formerly very rarely met with unground. The result was that it was rare to find even 25 casks (weighing about 12 cwts. each) of ground Dutch madder exactly alike. A recent improvement is that in Zealand, as well as in the Vaucluse, large works have been established, whose owners buy the roots from the small growers. Hence a quite uniform product is obtained in quantity. A very large proportion, both here and in the Vaucluse, is at once converted into garancine and other preparations. When the dry root has been stored a second time it is broken up and ground by edge-stones. The stones used in France are made of a kind of hard limestone. The excellent stone got from Belgium has been found to answer well. When ground the madder is carefully mixed, and packed in strong casks. Those from Zealand contain about 12 to 14 cwts., and those from Vaucluse 20 to 22 cwts. In Zealand adulteration is repressed by heavy penalties, and the maufactories are placed under proper inspection, so as to secure the purity of the article. This regulation has tended to support the Zealand madder in its severe competition with that of Avignon, where adulteration is not uncommon, as admitted by French authorities. There exists a considerable difference between the fresh root and the commercial madder, both in appearance and properties. When the recent root is squeezed an acid yellow liquid oozes out which turns red on exposure to the air. This fluid, when applied to cotton prepared with acetate of alumina, yields a bright red dye, which turns a dull rose-colour when soaped. The entire fresh root and its different parts yield duller and more fugitive shades than does the dried root. When a thin section of the fresh root is viewed under the microscope, not a trace of any separate colouring matter is seen. According to the researches of M. Decaisne the cells of the fresh root are filled with a yellow liquid, the deeper in colour as the plant is more mature. This liquid becomes converted into an insoluble red principle on contact with the air. It is a strange fact that the fresh madder has never been the subject of any other than chemico-microscopic research, on a very limited scale. After being ground the constituents of the root undergo important modifications, which go on even after it has been strongly compressed into the casks. We shall return to this subject after having considered the composition of madder.*

Kochlin found in 100 parts dry commercial madder† 55 parts of matter soluble in cold water; 3 parts soluble in boiling water, including the colouring matter; 1.5 soluble in alcohol; and 38 insoluble in the above liquids.

a. Substances Soluble in Cold Water .-

- I. Glucose, or at least a saccharine substance capable of fermentation, and of yielding an abundant precipitate with Fehling's test.
- 2. Cane-sugar, found at least in the Zealand and Alsace varieties. The amount varies with the age of the root and the circumstances of its growth, but cannot be estimated at less than from 13 to 16 per cent. Part of the glucose pre-exists in the root, but part, as is evident from the researches of Dr. Schunck, is formed by the splitting up of the glucosides which the root contains.

Neither of these sugars is of any use in dyeing. Both are sometimes utilised in the shape of alcohol, formed during the manufacture of flowers of madder.

- Gum and Mucilage.—The latter appears to be a pectate of potash. The cold aqueous infusion of ground madder from Zealand and Alsace often becomes a complete jelly from the abundance of this substance.
- 4. The aqueous solution of madder, like that of other vegetables, contains albumen.
- A peculiar nitrogenous principle precipitable by alcohol and acting the part of a ferment. It breaks up the colouring glucosides, and converts pectin into pectic acid (erythrozym).

^{*} In order to decide the question as to the effect of heat in drying madder in Zealand, a quantity of fresh root—about 1 kilo.—was carefully cleansed from earth, and placed, unbroken, under a bell-glass over sulphuric acid. The air of the glass was exhausted, and the pump worked daily for half an hour, to remove any air or vapour given off from the roots. After about three weeks the roots were quite dry, and, on being ground up, the madder was not found to differ from that prepared in the ordinary way. Its colour was paler, but its tinctorial power was at least equal.

[†] Madder is very hygroscopic, and may contain 17 per cent of water without feeling damp.

- Pectose.—According to Schützenberger, madder contains pectose, which
 he infers from the fact that on adding an aqueous solution of madder
 to solutions of pectin, the latter were speedily gelatinised.
- 7. Chlorogenin (Schunck), called rubichloric acid by Rochleder.

This substance is one of the immediate principles of madder and of a few other plants. When boiled with weak mineral acids it is decomposed, yielding a sap-green insoluble matter.

- 8. Alkaline Tartrates, Malates, and Citrates, according to Rochleder are found in the cold aqueous extract, though the Levant madders were asserted to contain citrates only. Dr. Schunck has never met with either tartaric, citric, or malic acid in madder, but with abundance of oxalic in their stead. He very justly remarks that in the older analyses of vegetable matters non-crystallisable acid syrups were commonly set down as "malic acid."
- We find, further, nondescript extractive matters with colouring glucosides, of which we shall treat below.
- ro. Alkaline sulphates, phosphates, and chlorides.

b. Substances Soluble in Boiling Water and in Alcohol .-

These comprise chiefly the colouring matters and resins, of which we shall speak subsequently.

The immediate principles insoluble in water and alcohol comprise 32 to 40 per cent of woody fibre, deduction having been made for the mineral constituents. This insoluble portion is made up of cellulose, free pectic acid, pectose, pectate, oxalate, carbonate, and phosphate of lime; phosphate of magnesia with silica, alumina, and oxide of iron. The study of the ash, both as to its quality and quantity, is of great importance, since it not only affords the means of detecting a certain class of adulterations, but bears upon the results obtained in dyeing with different kinds of madder. The ash, which is not easily obtained quite free from traces of organic matter, contains the mineral salts naturally present in the plant, and those formed by the decomposition of the salts of organic acids. Among the latter occur, therefore, carbonates of soda, potash, and lime. The composition of the ash varies, as might be expected, with the composition of the soil in which the madder is grown. The percentage differs also greatly. Chevreul found in 100 parts of Levant madder* 9'8 of ash, and in that of Alsace 9'5 to 12 and 13. According to Schlumberger, Avignon madder yields on an average 8.08 per cent of ash, and that of Alsace 7.20. Persoz (senior) found the following percentages, noting expressly that he employed pure nitrate of ammonia in order to burn off the last traces of carbon:-Alizari from Avignon, 8.1 to 8.03; racine from Alsace, 6.3 to 6.05; pure palud madder from Vaucluse, 9.6 to 10.72; rosée from the same district, 8.4 to 8.85. Alsace madder, 7.9 to 7.02. Girardin states that several experiments made by him with pure madder yielded only 5 per cent of ash. Notwithstanding this author's great authority, it is undeniable that his statement only refers to the

^{*} The question arises whether this has been madder, or racine. No roots are ground in the Levant or Barbary, and the root only comes into the market as "alizari," or "racine." "Marena" is only occasionally brought to Europe.

minimum of ash found in this substance. In some low-priced madders, contaminated with the earth and sand in which the roots have grown, the ash amounts occasionally to 50 per cent. Dried Zealand madder, very carefully incinerated, gave 7'20 to 9'5 ash on an average of some 50 estimations. The composition of the ash of madder varies. Schlumberger found in 100 parts—

Salts of po	otassium				 	 4.06
Silica .						-
Phosphate	of lime	and	alum	ina	 	 0.80
Carbonate	of lime				 	 3.20
Loss					 	 0.12
Total	ash					8:76

The same chemist found in 100 parts of Alsace madder-

Salts soluble in water		 	 4.53
Silica		 	 0.62
Alumina and phosphate	of lime	 	 1.33
Carbonate of lime		 	 0.87
Loss		 	 0.13
Total ash		 	 7:20

100 parts of Avignon madder yield 5.72 parts carbonate of lime, of which 2.77 pre-exist as bicarbonate, while the rest is formed by the ignition of organic salts of lime, from which latter source the small quantity of carbonate of lime met with in the ash of the Alsace madder is exclusively derived.

The results of the researches made by Kuhlmann, Bucholz, and John, all previous to the year 1826, are in some respects noteworthy, and may be briefly summarised here. Madder, according to Kuhlmann, contains—

- 1. A yellowish-brown colouring matter soluble in cold water.
- 2. A red colouring matter soluble in hot water.
- 3. Woody fibre.
- 4. Vegetable acid.
- 5. Mucilage.
- 6. Vegeto-animal matter.
- 7. Gum.
- 8. Sugar.
- o. Bitter principle.
- 10. Odoriferous resin.
- II. Ash, viz .-

Carbonate of potassa	 	 		0.008
Sulphate of potassa	 	 		0.033
Phosphate of potassa				
Chloride of potassium	 	 		0.403
Carbonate of lime	 	 		0.462
Phosphate of lime	 	 	0 0	0'082
Silica	 	 	9 4	0.030
Loss	 	 		0.031
				1.380

Accordin

Buch	nolz fou	nd in 100	parts of	air-dried	madder-

10	und in 100 parts of air-dried ma-	uuei-	_		
	Red extractive matter				39.00
	Brownish red matter soluble in al alcohol	lkali e	s an	d}	1.09
	Acrid extractive matter				0.06
	Red fatty resin			- +	1.03
	Brownish red gum				9.00
	Woody fibre				22.02
	Matter soluble in caustic potash				4.06
	Vegetable salts of lime				1.08
	Moisture				12.00
	Loss				7.04
				-	
					100.00
0	to John, 99 parts contain-				
	Brown-red wax-like substance				1.00
	Red resin				3.00
	Red extractive matter	* *			12.00
	Oxidised extractive				5.00
	Brown gum				8.00
	Woody fibre				42.02
	Acetates of potassa and lime			4.0	8.00
	Phosphate, sulphate, and cl	hlorid	е	of	7:00

.

Silica

Oxide of iron

7'05

I'05

0.02

The varieties of madder from different localities behave in the dye-beck in a perceptibly different manner. This appears partly due to the special nature of the colouring matter contained in each variety. It is, therefore, useful to study each kind separately. Since there is on this subject wide divergence of opinion both among scientific and practical men, we premise the following principles: -I. The fresh root contains its tinctorial principles in another form from the ground madder which has been kept for some months. In the former state the colouring matters are in some combination which renders them soluble in water, but the moment the juice of the root is in contact with the air this state is modified. 2. The soluble combination of the madderpigments is of the same kind as those which chemists know under the name of glucosides. The experiments made by E. Koechlin, Decaisne, Watt, Robiquet, Colin, Kuhlmann, Higgin, and Runge, fully prove the existence of soluble colourable* matters in the fresh root as well as in the powder met with in commerce, though the quantity decreases with the increasing age of the madder.† The researches of these chemists throw no light upon the precise nature of these substances. We shall review the labours of the authorities named, and compare them with the results of Schunck and Rochleder. Watt, while operating upon Zealand madder, observed that cold water takes up

^{*} Such as are under certain circumstances capable of forming pigments and dyes.

[†] No satisfactory explanation has been given for the well-known fact that madder improves in the cask. This is most marked in Zealand madder, which reaches its perfection after twenty months, and is still excellent after thirty-two. Avignon madder is spoiled much earlier

from that substance a certain amount of colouring principle. Recent Zealand madder-root, provided it be unbroken, can be washed with cold water without the slightest loss of colouring matter. The experiment was made upon 2 kilos. of fresh root, carefully cleaned from adhering earth with a sponge. When an aqueous infusion of madder is slowly evaporated in an open vessel exposed to the air there is formed on the surface of the liquid a pellicle, which soon sinks to the bottom, and is succeeded by the appearance of another, which goes on until the whole is evaporated to dryness. The extract thus formed is only in part soluble in water. From the experiments made by Robiquet and Colin while preparing pure alizarin from Alsace madder, it follows that in this madder at least a portion of the alizarin is present in a state soluble in water.* The quality of the water may seriously affect the results of such experiments. Experiments instituted some years ago with fresh Zealand madder and Zealand racine in sufficient quantity (5 kilos. of each) show that cold water does not appear to extract any of the tinctorial matters. With ground madder it is different. On drying the substances previously experimented with very carefully, powdering and dyeing with them against standard samples of madder of known tinctorial value, no inferiority was found in the roots. On submitting them to analysis, the quantity of alizarin found did not differ from that extracted from roots treated as usual. The abovementioned chemists mixed I part of madder with 3 parts of water, filtered and pressed the substance upon a piece of cloth, and obtained a red-brown liquid, which in about ten minutes was converted into a jelly. This was found to be a mixture of pectic acid and gelatin, which had become insoluble. As far back as 1823, Kuhlmann observed that madder contains a yellow colouring matter, very soluble in water, which he named Xanthin. He obtained this xanthin by exhausting madder with boiling alcohol, evaporating the solution to dryness, and taking up the dry residue with water, which dissolves the xanthin, and leaves any alizarin that may have been extracted undissolved. The fluid is first filtered, then acetate of lead is added, whereby a brownish matter is precipitated. This is removed by filtration, and to the filtrate baryta-water is added, whereby a precipitate is formed, containing xanthin combined with oxide of lead. This precipitate is thoroughly washed, and, after having been suspended in pure water, is decomposed with very dilute sulphuric acid. The sulphates of lead and baryta having been removed, the liquid is evaporated to dryness, the dry residue taken up with alcohol, and again evaporated. The xanthin is then left as a viscid, bright orange-coloured substance readily soluble in water. It has a sweetish bitter taste, and is soluble in alcohol, but insoluble in ether. Alkalies turn it red. Neither the neutral nor the basic acetate of lead gives a precipitate with this substance. It dyes mordanted cotton a bright orange. It is decomposed by strong sulphuric acid, yielding chlorrubin, so that this substance is a mixture of at least two substances as well as glucose. Zealand, Alsace, and Avignon madder contain far more xanthin than the madder from the Levant and Barbary.

Runge obtained a yellow soluble substance by exhausting Zealand madder with sixteen times its weight of water, and precipitating the solution with

^{* &}quot;Annales de Chimie et de Phys.," t. xxxiv., p. 225; and "Bulletin de la Soc. Indust. de Mulhouse," t. i., p. 108. 1828.

lime water. This precipitate is decomposed with acetic acid, and the solution boiled with wool mordanted in alum to remove purpurin. The solution is evaporated to dryness, taken up with alcohol, and again precipitated with an alcoholic solution of acetate of lead. The precipitate thus obtained is washed with alcohol, and decomposed with sulphuretted hydrogen.*

Higgin exhausts madder with boiling water, precipitates the matters sparingly soluble in water with very dilute sulphuric acid, saturates with carbonate of soda, and afterwards digests the fluid with hydrate of alumina, in order to separate alizarin. Baryta water is next added, and afterwards subacetate of lead. The precipitate is well washed and decomposed with sulphuretted hydrogen. The product thus obtained still contains chlorogenin, since on being boiled with acids a green precipitate ensues.

According to Schunck, the aqueous extract of madder, made either with cold or tepid water undergoes spontaneous decomposition, either with or without access of air. A flocculent yellow precipitate is formed, which contains all the colouring matter of the infusion. Schunck ascribes the bitter taste, and the tinctorial properties of the extract, to a substance which he names Rubian, and considers the xanthin of Kuhlmann, Runge, and Higgins to be a mixture of rubian, chlorogenin, and glucose. Rubian, properly prepared, is a hard, amorphous, brittle substance, glossy when in thin laminæ. Its colour is deep yellow, or brown when seen in large masses. It is permanent in the air, easily soluble in water, sparingly in alcohol, and insoluble in ether. It has an intensely bitter taste. The aqueous solution is precipitated only with subacetate of lead. With concentrated sulphuric acid rubian yields a blood-red solution, decomposable by heat. Nitric acid does not affect cold solutions of rubian, but, on boiling, phthalic acid is formed. Normal phosphoric acid and the organic acids are without any action upon rubian, even at the boiling-point. Soda converts the yellow solution to a blood-red, which, on boiling, becomes purple. Acids then precipitate from the solution a reddish-orange substance, and the liquid becomes colourless. At a higher temperature the glucoside which forms the rubian is split up. Ammonia also modifies the yellow solution to blood-red, but no further change ensues on boiling. Lime and baryta water throw down rubian as a deep red substance, soluble in water. Magnesia converts the yellow solution of rubian to a deep red, the alkaline earth becoming dissolved. Carbonates of lime and baryta have no action; alumina and the hydrated peroxide of iron and oxide of copper throw down rubian completely from its solutions. In presence of an alkali, rubian reduces the salts of gold, but salts of silver and copper are not acted upon under the same conditions. Rubian fuses when heated, and burns on ignition, leaving from 6 to 8 per cent of ash, consisting of carbonate of lime. If heated to 130° C. in a tube, it yields orange vapours, composed chiefly of alizarin. When rubian is boiled with dilute hydrochloric or sulphuric acid it yields, on cooling, a flocculent orange matter, insoluble in these acids. In the liquid there remains a kind of sugar capable of fermentation and of reducing alkaline solutions of copper. Rubian undergoes a similar decomposition by the action of a peculiar nitrogenous compound which exists in madder, and

^{*} It should be kept in view that too many of those who have experimented with madder have entirely forgotton two essential points:—To ascertain the time that the sample had been in cask, and the precise locality and manufactory from which it originated.

is called erythrozym.* This ferment may be obtained by the addition of alcohol to an aqueous infusion of madder, when a curdy precipitate is formed. If this is added to a solution of rubian, the latter in the course of a few hours becomes a bright brown jelly, containing the tinctorial principles in an insoluble state. Rubian is very difficult to obtain pure, being very liable to decomposition and not precipitable by any metallic salt, except the subacetate of lead. The separation of rubian from chlorogenin requires very nice manipulations. To effect this separation Schunck makes use of the great affinity of rubian for porous bodies, especially animal charcoal. He digests a hot decoction of madder with animal charcoal, and washes the latter on a filter with cold water until a small quantity of the washings, when boiled with hydrochloric acid, ceases to yield a greenish colouration. Thus the chlorogenin is removed. The charcoal is next exhausted with boiling alcohol, which extracts the rubian. The alcoholic solution is evaporated to dryness, taken up with water, again treated with animal charcoal, and the latter again exhausted with alcohol.

This treatment is repeated until the chlorogenin is entirely removed. The alcoholic solution is finally evaporated to dryness, taken up with water, and this aqueous solution is first treated with a solution of neutral acetate of lead, which precipitates any impurity. It is filtered, and then precipitated with basic acetate of lead. The precipitate formed is decomposed with sulphuretted hydrogen or dilute sulphuric acid, and after removal of the lead compound rubian is left dissolved in the water. The substance in this state still retains mineral matter, and is therefore not quite pure. Nevertheless, we may draw conclusions regarding the tinctorial matter pre-existent in the madder root during its growth. Rubian is a glucoside, or perhaps a mixture of glucosides, capable of being decomposed by acids, alkalies, and ferments into colouring matters and sugar. Since Dr. Schunck's analysis shows the formula to be $C_{10}H_{16}O_8$, the following equation represents the reaction which takes place:—

$$\underbrace{C_{16}H_{16}O_8 + H_2O = \underbrace{C_{10}H_6O_3}_{Alizarin,} + \underbrace{C_6H_{12}O_6}_{Glucose.}}_{Glucose.}$$

We shall presently see that the constitution of rubian is scarcely so simple. It probably contains several glucosides capable of yielding alizarin and pseudo-purpurin, &c. The composition of all these colouring matters approaches closely that of alizarin. Schunck has never found purpurin among the products of decomposition of rubian, whether this was affected by an acid, an alkali, or a ferment. He always, however, found a yellow crystalline colouring matter, first discovered by Runge, and named by him "madder orange." The nature of this colouring matter varies according to the agent employed, or rather, acids give rise to one substance, alkalies to another, and ferments to a third. These three substances, though essentially distinct, have some properties in common. Two of them, rubiacin and rubiadin, can easily be identified by their reactions. Rochleder's researches are chiefly valuable from the fact that he has succeeded in isolating the alizarin-glucoside in a crystalline state, and has named it ruberythric acid. It occurs mixed up with rubian.

^{*} The nitrogenous principles met with in madder are extremely prone to change, and are in this respect as difficult to study and to obtain in a pure state as some of the biliary principles. It is always the molécule en mouvement, and hence its protean properties.

A hot decoction of sliced Levant madder-root is treated successively with neutral and basic acetate of lead. The second precipitate, after being thoroughly washed, is decomposed with sulphuretted hydrogen. The sulphide of lead is well washed with cold water, which removes phosphoric and rubichloric acids, leaving almost the whole of the ruberythric acid along with the sulphide of lead. The lead compound is next thoroughly exhausted with boiling alcohol, and the solution thus obtained concentrated by evaporation on the water-bath. The residue is taken up with water; a little baryta-water is added, and the precipitate thus produced is filtered off. More baryta-water is added, in order to throw down the ruberythric acid as a deep cherry-red flocculent ruberythrate of baryta. This is dissolved in dilute acetic acid, the solution nearly neutralised with ammonia, and then precipitated with basic acetate of lead. The cinnabar-red precipitate thus obtained is suspended in alcohol, decomposed with sulphuretted hydrogen, boiled, and filtered hot. On cooling, ruberythric acid is deposited in bright yellow, silky, prismatic crystals. It is very soluble in ether, alcohol, and hot water, but sparingly in cold water. It bears, in many respects, a great likeness to rubian. By mineral acids it is split up into sugar and alizarin.

The researches of Kopp on the colourable glucosides are very interesting.* He treated Alsace madder, about six months old, with a saturated solution of sulphurous acid. By this means the peculiar action of the ferment present in the madder is arrested, and the colouring matters present are eliminated in a soluble condition. The filtrate is yellow, and on the addition of 2 to 3 per cent of hydrochloric acid, and heating to 60° C., a flocculent red matter is thrown down not containing a trace of alizarin. On raising the temperature to the boiling-point alizarin is thrown down mixed with chlorrubin. The alizaric glucoside is therefore more stable than the other glucosides. The aqueous solution of madder, treated with dilute sulphurous acid, shows, after pressure and filtration, the following properties:—The concentrated liquid is deep orange, with a brownish shade. The taste is faintly acid, mixed with a sweetish bitter. Notwithstanding the smell of the sulphurous acid, the characteristic odour of madder is quite distinct. In closed vessels this solution remains unaltered for a long time. Sometimes a brownish, light, flocculent deposit forms. If the solution of sulphurous acid employed is contaminated with hydrochloric acid there is deposited, in five to eight days, a semicrystalline mass of purpurin, of a bright vermillion-red. Since this deposit is very heavy, it can easily be removed by decantation. If the fluid containing sulphurous acid is exposed to the air it loses its odour, and grows turbid. A pulverulent greyish-black substance is deposited, and the liquid becomes discoloured. Decomposition sets in, and when ammonia is added there is no longer a beautiful violet-red, but a dirty muddy appearance. This solution of madder in sulphurous acid behaves with reagents as follows: -With potash, soda, and ammonia, no precipitate, but a violet-red colouration with a yellowish tinge. If the alkaline solutions are very concentrated a precipitate is formed on boiling. The liquid retains its original colour as produced by the addition of an alkali, and a portion of the precipitate is re-dissolved on the addition of water. Nothing is at first produced by the addition of hydrochloric acid, but

^{*} E. Kopp, "Répertoire de Chimie Appliquée," tome iii., p. 85, and "Bulletin de la Société Industrielle," tome xxxi., p. 145.

RUBIAN.

after some time a yellowish-red or brownish precipitate of purpurin is formed. The same happens when nitric acid is substituted for hydrochloric acid. In both instances this fluid remains orange-yellow. Oxalic acid produces no immediate change, but after a time there is formed a pale yellow flocculent precipitate containing oxalate of lime. The colour of the fluid is not altered. No reaction is produced by the addition of alkaline chlorides, or of the chlorides of the alkaline earths. Carbonate of soda gives no precipitation, but colours the fluid purple. Lime-water yields immediately a brownishcrimson precipitate, and the colour of the liquid turns a reddish-violet. If the precipitate is filtered off, and heat applied, another precipitate of a rose-red is produced. Solution of alum produces no change at first, but after a time a brilliant vermillion precipitate is produced, the supernatant liquor remaining a yellowish-red. If a large excess of solution of alum is added, and a solution of carbonate of soda or lime-water immediately after, a rose-red precipitate is obtained, which, when dry, exhibits a very pure rose-colour, especially if limewater has been employed. The acetate and the hyposulphite of alumina give similar reactions. The precipitation of this alum-lake is promoted by heat. Its shade depends very much upon the relative proportions of the ingredients, and upon the concentration of the madder-liquor. With hypochlorite of lime the liquid is bleached to a yellowish colour, and a light flocculent precipitate is deposited. A solution of protosulphate of iron gives a deep brown precipitate, the liquid assuming a deep-somewhat inky-colour. With perchloride of iron no immediate precipitate is formed; the liquid turns a deep brownishyellow, and after a time a brownish-black precipitate is deposited. Perchloride of tin gives an orange-yellow precipitate. With acetate of lead in moderate quantity there is formed a chamois-coloured precipitate, the liquid retaining its orange-yellow colour. If the precipitate first formed is removed, and a further quantity of the same reagent is added, a yellowish-red precipitate is produced, and the supernatant liquid retains only a slight yellowish colour. On the addition of ammonia to this liquid a fine rose-red precipitate is produced. Corrosive sublimate gives a flesh-coloured precipitate, whilst the liquid remains yellow. If the mercuric salt has been previously acidified with hydrochloric acid no immediate precipitate is formed, but after a time an orange-red precipitate is deposited, which is almost entirely soluble in boiling

Secondary colouring matters, either insoluble or but very sparingly soluble in water, are derived from the decomposition of the above-mentioned substances. On this subject there has been much controversy; for while no one denies the existence of alizarin, some assume the presence of one or more distinct tinctorial substances, whilst others hold these to be merely alizarin in a more or less impure state. This last view gained strength from the fact that the physical, chemical, and tinctorial properties of alizarin are very readily modified and masked by the presence of small quantities of heterogeneous matter. Thus, as long as alizarin retains traces of a resinous facty matter which clings to it very persistently, it yields in alcohol a brown solution, and cannot be obtained in well-defined crystals. When pure it dissolves in alcohol with an orange colour, and forms long needle-shaped crystals. The large number of colouring matters which, according to Schunck, are derived from rubian, did not appear to many investigators of this subject sufficiently well defined to be accepted without some hesitation.

Since the researches of Persoz, Gautier de Claubry, Runge, and others, the existence of another red pigment, purpurin, has been admitted. It differs from alizarin by the purple colour of its alkaline solution, whilst alizarin yields violet-blue solutions. Kopp subsequently succeeded in producing, on a manufacturing scale, a preparation containing no alizarin, and exhibiting all the characters of purpurin. One kilo. of this product represents about 60 kilos. of Alsace madder. It was carefully investigated by Schiffert and Schützenberger. They considered the existence of the following colouring matters as decided: - (1), alizarin; (2), purpurin; (3), pseudopurpurinthese three are either red or orange, and yield red shades with aluminous mordants; (4), an orange matter which likewise yields, with aluminous mordants, a red shade; (5), a yellow matter, xanthopurpurin (not to be confounded with Kuhlmann's xanthin), yielding, with aluminous mordants, yellow shades.

The existence of the three last colours mentioned by Schützenberger is considered by Schunck more than doubtful. They are either mixtures or are identical with substances previously known. The yellow colour has exactly the same percentage composition as rubiacin. The latter is distinguished from all the other madder colours by dissolving in per-salts of iron with a purple or brownish-red colour; this simple test would have decided the identity or distinction of the two bodies. The practice of giving little more than analyses of new substances without any account of their characteristic

reactions is highly objectionable.

Alizarin, or lizaric acid, is the most important and the most valuable colouring matter contained in madder. It is the only one which yields fast dyes capable of resisting the operation of cleansing. By a series of experiments made by Schützenberger with variously-mordanted cloths, submitted afterwards to dye-becks containing madder and its commercial preparations, it has been fully proved that in these dyed shades-Turkey-red includedalizarin alone is present. Hence it is inferred that alizarin pre-exists in the madder-root, and is not a product of any subsequent decomposition.

Alizarin is readily obtained in crystals, both by sublimation and by the evaporation of its solutions. It is procured as hydrate by the slow evaporation of its ethereal solution. In this state alizarin has the appearance of micaceous plates of a golden-yellow lustre, not unlike mosaic gold. At 100° C. it loses 3 equivalents of water. The anhydrous crystals exhibit brilliant prismatic needles of a red tint, verging upon yellow. These crystals are best obtained by sublimation at 240° C., or by deposition from strong boiling alcohol not containing more than 14 per cent of water. This process only yields good crystals with alizarin that has once, at least, been purified by sublimation. It can also be obtained by crystallisation from water, in a sealed tube, at 250° or 280° C., or, better still, by the use of a mixture of 9 parts of water and I part of alcohol.

Alizarin fuses at 215° C., and sublimes between 215° and 240°, but if kept for a long time at 100° C. it slowly evaporates, more readily if placed in a current of water or of steam. If it is desired to sublime alizarin without decomposition, it should be heated in small quantities only. The best method of subliming alizarin, from impure alizarin, alcoholic madder extract, extract of garancin, or any other substance containing alizarin, is to place the substance to be operated upon at the bottom of a small porcelain capsule capable

REACTIONS OF THE COLOURING PRINCIPLES OF MADDER.

Purpuroxanthin.	Orange matter.	Pseudopurpurin.	Purpurin.	Alizarin.		Name.
No bands.	No bands.	Same as above.	One band near red, another near yellow.	Two bands near red. Long orange needles.		Spectroscope.
Yellow needles crystallised from alcohol and ben-	Small groups crystallised from alcohol.	Fine brick-red needles crystal-lised from ben-zol.	Red needles.	Long orange needles.		Crystallisation.
Sublimes.	Decomposes, and yields purpurin.		Sublimes with decomposition.	Sublimes readily.		Effect of Heat.
Yellow solution.	Red solution.	Red solution.	Red solution.	Bluish-purple so- lution.	Alkalies.	
Soluble.	Insoluble.	Soluble.	Soluble.	Soluble.	Benzol.	Solubility in
Soluble.	Readily soluble.	Very slightly so- luble.	Same as above.	More soluble in hot than cold.	Alcohol.	

zol.

of containing 50 grms. A few decigrms of material are sufficient for the experiment. A piece of clean white filtering-paper is placed on the top of the capsule, which is next covered with its lid and heated on the sand-bath to 250° C. After the lapse of half an hour the interior of the capsule will be found lined with long, beautiful needles. At the bottom there remains a porous, bulky, carbonaceous substance, containing hardly a trace of alizarin, when pure alizarin has been experimented with. When alcoholic extract of madder or garancin has been submitted to sublimation the alizarin is often soiled by empyreumatic substances, and requires to be re-sublimed. The colour exhibited by alizarin varies according to the conditions under which it has been obtained. It is sometimes a dark red substance, usually rather orange, but sometimes yellow, especially if it is crystallised from an acid solution, -as, for instance, when glacial acetic acid has been applied. Pure cold water only dissolves an insignificant trace of alizarin, but if the water contains any alkaline matter it becomes yellowish or orange by a trace of alizarin. According to Plessy and Schützenberger, 100 parts of water, at 100° C., dissolve 0.034 part of alizarin; at 150° C., 0.035; at 200° C., 0.82; at 225° C., 1'70 parts; at 250° C., 3'16. Up to 200° C., therefore, the solubility increases slowly, but becomes far greater on approaching the subliming point of alizarin. The solubility of alizarin in alcohol is not perfectly determined. At the ordinary temperature of the air it is more soluble in alcohol than in water. When pure, a boiling alcoholic solution of alizarin exhibits an orange-yellow colour, and on cooling deposits long needle-shaped crystals. Alizarin is readily soluble, especially with the aid of heat, in ether, wood-spirit, benzol, oils of tar, naphtha, and petroleum, spirits of turpentine, sulphide of carbon, glycerine, chloroform, and acetic acid. The hot saturated solutions of some of these deposit alizarin in crystals on cooling. An aqueous solution of alum does not, when cold, dissolve any alizarin. It dissolves to some extent in a hot solution, but is re-deposited on cooling. Strong sulphuric acid dissolves alizarin without decomposition or change. Water precipitates the colouring matter from this solution unaltered, in the shape of an orange flocculent precipitate. The solution of alizarin in sulphuric acid is not affected by a temperature of 200° C. As regards the composition of alizarin and the formulæ assigned it various views prevail. That given by Dr. Schunck, C14H10O4, agrees best with the analysis of pure specimens, and is confirmed by the experiments of Graebe and Liebermann on the artificial formation of alizarin. Schunck deduced his formula from the examination of rubianic acid, the glucoside of alizarin. This acid gives a potash salt crystallising in needles, by means of which the above-mentioned chemist was enabled to determine the atomic weight of the acid. It contained C26, and hence alizarin must have C14. Many chemists were led astray by supposing, with Laurent, that there must be a close relationship in composition between alizarin and naphthalin.

Alizarin is a weak acid capable of combining with bases. With alkalies it yields salts readily soluble in water, sparingly soluble in alcohol, and insoluble in ether. The aqueous solutions exhibit a splendid violet-blue colour. Crystallised alizarate of soda is readily obtained by adding an alcoholic solution of soda to alcohol in which alizarin is kept suspended, and immediately after adding a quantity of ether to the mixture, so that it may form a separate

layer. The whole should then be kept for some time in a well-closed vessel, and left standing undisturbed. The ether slowly mixes with the rest of the fluid, and the alizarate of soda separates in the shape of needles. The alkaline earths and metallic oxides yield, with alizarin, compounds insoluble in water, and which are violet, red, or black. Some of these are technically known as lake-colours. Those of alumina are red or rose-coloured, whilst those of peroxide of iron are violet or black. The true composition of these salts is but imperfectly known. The carbonates, phosphates, pyrophosphates, borates, silicates, oleates, and generally all the salts capable of turning red litmus-paper blue, dissolve alizarin, especially with the aid of heat, yielding reddish-violet coloured solutions. Liquid ammonia acts upon alizarin in a very peculiar manner, which reminds us of the behaviour of carminic acid under similar circumstances. Ammonia first dissolves alizarin, yielding a characteristic solution of a violet-blue colour. From this solution acids throw down the alizarin unchanged, in the shape of yellow flocks. But if the solution is kept in a closed vessel for at least twelve hours, at a temperature of 100° C., or preserved for several weeks at common temperatures, acids no longer precipitate it as before, but cause the appearance of a deep violet flocculent mass, containing the elements of alizarin and ammonia combined in so stable a manner that even strong acids do not cause its decomposition. This substance—called by its discoverer, Schützenberger, alizaramide or alizareine is formed without contact of air, and without the action of oxygen. In a wet state it is of a reddish-violet colour, but when dry quite black. It is perceptibly soluble in water and in alcohol, even when dilute, yielding a beautiful violetred solution. It is also soluble in ether. On evaporation of the alcoholic solution it is obtained in crystals. If heated on platinum foil it burns without sublimation. When boiled with caustic alkali, alizarinamide gives off ammonia, but no ammonia is evolved when it is rubbed up with dry caustic lime in a mortar. Cloth, previously mordanted and then dyed with this substance, assumes colours somewhat similar to those yielded by madder, though less rich, and accompanied by a pale violet hue. Wool is dyed by this colour of a dirty lilac, without the aid of any mordant.

When alizarate of soda, in crystals, is heated in a sealed tube to 120° C., along with iodide of ethyl, an ethylic derivative is obtained of a bright yellow,

insoluble in water and soluble in alcohol.

Chloride of benzol acts upon alizarin at 190° C. Hydrochloric acid is given off, and a compound formed which is insoluble in water, soluble in alcohol, but insoluble in ammonia at ordinary temperatures. When boiled with alkalies it is saponified, the result being the formation of an alkaline benzoate and alizarate.

Alizarin is readily acted upon by oxidising agents. Nitric acid and perchloride of iron convert it into phthalic and oxalic acids.

The action of reducing agents upon alizarin has not been fully investigated. If an alkaline solution of alizarin is heated along with aldehyd the violet liquid turns orange, and on the addition of an acid a yellow flocculent precipitate falls. Nascent hydrogen discolours the solutions of alizarin.

According to the recent researches of Graebe and Liebermann, alizarin, treated with powdered zinc and hydrochloric acid, yields a hydrocarbon—anthracen. Starting from this discovery the authors have devised a method

for the artificial production of alizarin, to which we shall recur elsewhere in full.

The preparation of pure alizarin from madder, on the large scale, is a tedious operation. The best material to start from is an alcoholic extract of good madder. Some kinds of this extract are manufactured on a large scale. When properly prepared they deposit a red granular substance, very suitable for the preparation of alizarin.

Another source is the "Green Alizarin" of commerce, first prepared by Kopp. To obtain it on the large scale madder is mixed with ten times its weight of aqueous sulphurous acid, to which a little hydrochloric acid has been added to decompose the lime-salts of the madder. The mixture is placed in a well-covered wooden vessel, and allowed to stand from twelve to twenty-four hours, with occasional stirring. The semi-fluid mass is thrown upon a filter, the vat is washed out with a little water, and the rinsings added to the filter; the liquid is allowed to run through, and the residue is strongly pressed. The liquid is again put in a wooden vat. The dry pressed residue is again treated with ten times its weight of sulphurous acid water, as before, the filtrate and the pressings being mixed with the first liquid. This treatment is repeated a third time, but the liquid obtained, being too weak to be mixed with the preceding, is saved for the second extraction of a fresh quantity of madder.

On adding to the sulphurous liquid about 3 to 5 per cent of sulphuric or hydrochloric acid, and heating to 60° C., an orange flocculent precipitate falls. Its precipitation is complete in about thirty minutes. The deposit is separated from the mother-liquor by decantation or filtration, and washed with a little cold water till the washings have a faint yellow colour and display no longer an acid reaction. This precipitate is purpurin, almost chemically pure. If the mother-liquor is now allowed to boil for two hours the so-called green or crude alizarin separates out, and is deposited in twenty-four to thirty hours as a greenish-black mass. It is washed by decantation with cold water two or three times.

From this so-called "green alizarin" a much purer article, "yellow alizarin," is obtained by the following process:—I part of green alizarin is boiled with 15 to 20 parts of rectified petroleum, boiling at 150° C. As soon as the boiling ceases the green insoluble matter separates as a sediment. After a few minutes the liquid is decanted. It contains much alizarin, part of which separates out on cooling. When the temperature has fallen to about 100° C., dilute caustic soda-lyc is added, and the mixture well agitated. The soda takes up all the alizarin, with a bluish-purple colour, whilst the petroleum becomes almost colourless, and may be used again. The lye is poured into dilute sulphuric acid, when alizarin separates in yellow flocks. These are collected on a filter, washed till perfectly free from acid, and dried. From this "yellow alizarin" pure alizarin can be prepared by sublimation.

Another suitable source for pure alizarin is cotton which has been dyed a Turkey-red. Several yards of this cloth are cut up and submitted to the action of alcohol, at 85 per cent, mixed with strong sulphuric acid. The fatty matter, alumina, and colour are simultaneously dissolved. The liquid thus obtained is very carefully neutralised with ammonia, by which the alumina is precipitated. After filtration the filtrate is concentrated on the water-bath, and

mixed with water. This throws down a mixture of fatty matter and tinctorial substance. This precipitate is dried, and exhausted with rectified bisulphide of carbon, which removes the fat. Alizarin remains behind almost pure, and may be further purified, either by sublimation in a porcelain capsule, by means of steam, or by the vapour of a mixture of 9 parts water and 1 part alcohol. The alizarin obtained from Turkey-red is so pure that it can be sublimed leaving scarcely any residue. When madder extracts have been employed as the raw material the sublimed alizarin is contaminated with empyreumatic products, which have to be removed by washing with cold alcohol and recrystallisation from a hot alcoholic solution.

Alizarin yields, with aluminous mordants, red and rose shades, which are extremely fast, resisting the action of light, boiling soap-lyes, and even dilute nitric acid. After this treatment, technically known as clearing (avivage), the colour is a bright full red, or a rose with a slight bluish reflection. With iron mordants alizarin yields solid blacks and violets of great beauty. The tinctorial power of pure alizarin is about ninety times greater than that of good madder. To dye with pure crystalline alizarin it should be first rubbed up in a mortar with some alcohol, and the mixture poured into water to which some chalk has been added. No perceptible action takes place till the temperature has been raised to 70° or 80° C., and the alizarin begins to dissolve. To exhaust a dye-bath containing alizarin the quantity should not be very great, and excess of water should be avoided; 15 decigrms. of alizarin to 250 cubic centimetres of water are sufficient. This colour-bath, into which the mordanted fabric is now plunged, should be kept at nearly the boiling-point of water, by being placed upon the water-bath. The process of dyeing should be continued till the liquid has been nearly evaporated to dryness. This is the only satisfactory mode of testing the relative value of samples of alizarin. According to the experiments of Schützenberger the fabric thus dyed contains

Artificial alizarin is described in the section treating of coal-tar colours.

mordant applied.

a lake of madder, which is red, rose, violet, or Turkey-red, according to the

Purpurin.

As early as 1828 the researches of Robiquet, Persoz, and others, pointed to the presence in madder of a tinctorial principle distinct from alizarin. It was first prepared by treating Avignon madder with concentrated sulphuric acid, taking care to avoid too great rise of temperature during the operation. This material, known in commerce as charbon sulphurique, is then well washed with water to remove acid, and next boiled for a quarter of an hour with an aqueous solution of alum, containing 12 per cent of that salt. The liquid is filtered while boiling, and to the filtrate I part of sulphuric acid is added. On cooling, a red flocculent matter is thrown down along with crystals of alum. It is collected on a filter, and washed with pure cold water. The quantity of sulphuric acid required for the preparation of the charbon sulphurique varies with the kind of madder and the scale of the operation. If a kilo. of Alsace madder is taken, half that weight of sulphuric acid is sufficient. If only 25 or 30 grms. of the same madder are operated upon, 3 or 4 parts of acid are required. The effect produced by the acid is the destruction of such mucilaginous and other matter as would render the subsequent washing of the

madder difficult and tedious; though it would be an improvement to wash the madder first with water. Purpurin, as obtained by this process, still contains alizarin, but it is distinguished from that substance by its greater solubility in water, to which it imparts a fine rose-colour. Keechlin obtained from 90 parts of madder 4.5 of purpurin. Claubry and Persoz mix the madder with water to a thin paste, and add, for every kilo. of dry madder, 90 grms. of sulphuric acid. The mixture is next boiled by means of steam blown into it with leaden pipes. The material is thrown on a filter, washed with water, and the residue treated first with carbonate of soda, which dissolves a red colouring matter (alizarin?), and afterwards with a boiling solution of alum. To this latter solution sulphuric acid is added. A flocculent orange matter is thrown down, which, after treatment with alcohol and ether, yields crystalline needles, called by the above-named chemists "madder-rose." It is distinguished from alizarin by its greater solubility in alum, and its insolubility in protochloride of tin.

Runge and Debus boil the madder, previously washed, with alum-water, filter, and let the filtrate stand for some time, to permit of the precipitation of the alizarin. This is removed by a second filtration, after which the rosecoloured liquid is precipitated with sulphuric acid. The flocculent matter thus thrown down is washed with water, boiled in dilute hydrochloric acid, and dissolved in boiling alcohol (85 per cent). On cooling, a crystalline matter is precipitated, which is purified by repeated crystallisation from alcohol and ether. Wolff and Strecker employ a similar mode of preparation, but mix the madder previously with water, and allow it to undergo fermentations, after which they wash again. Whilst thus experimenting they did not obtain a trace of alizarin. Their inference that the alizarin was converted by fermentation into purpurin has been proved to be incorrect. They propose, as a method for separating alizarin from purpurin, to combine both with hydrate of alumina, and to boil this lake with carbonate of soda, which dissolves purpurin. This operation may be conducted as follows:—The aqueous decoction of madder is precipitated with sulphuric acid, the resulting precipitate extracted with boiling chloride of aluminium, and the colours thus dissolved reprecipitated with hydrochloric acid. The precipitate is washed, boiled with hydrate of alumina, and then boiled with a solution of carbonate of soda.

The most elegant, and at the same time most practicable, method of preparing pure purpurin, free from alizarin, has been devised by Kopp, and is carried out on the large scale by Schæraff and Lauth:—600 lbs. of ground madder are allowed to steep for ten hours, in a vat containing 800 to 1000 gallons of a solution of sulphurous acid, and, after running off this liquid, the madder is again treated with 200 to 250 gallons of the same acid solution. These liquors are then mixed with 3 per cent of sulphuric acid, at sp. gr. 1.60, and the whole is treated as described under the preparation of "green alizarin."

Schiffer and Schützenberger have investigated purpurin thus prepared, and pronounce it a well-defined chemical substance and a natural constituent of madder, and not alizarin soiled by some foreign matter. Having operated upon some 500 grms. of the commercial purpurin, they have found it to contain two red colouring substances, viz., purpurin properly so-called, and pseudopurpurin, besides an orange and a yellow tinctorial body. Each of these substances was obtained in a crystalline state, exhibiting distinct characters,

and a perfectly definite elementary composition. The separation of these substances is based upon their varying solubility in alcohol and benzol. The yellow and orange principles are very soluble in luke-warm alcohol at 85 per cent, wherein purpurin and pseudopurpurin are nearly insoluble. The yellow is soluble in benzol, in which the orange is insoluble. Purpurin is tolerably soluble in boiling alcohol, from which, on cooling, it is deposited in crystals, whilst pseudopurpurin is almost insoluble in the same liquid. The yellow matter, xanthopurpurin, is contained in commercial purpurin in small traces only, not exceeding 1 part in 500. The orange matter and purpurin proper form about one quarter of the commercial substance in equal proportions, whilst the entire residue is made up of pseudopurpurin. To obtain pure purpurin the easiest method is to place a little of the commercial product in a porcelain capsule, and to treat it on the sand-bath as already directed for alizarin. Purpurin only sublimes, leaving a bulky carbonaceous mass at the bottom of the capsule. During the sublimation pseudopurpurin and the orange matter are partly converted into purpurin. Another method is to heat commercial alizarin, previously well washed with luke-warm alcohol, in a sealed tube along with alcohol up to 200° C. By this process purpurin is obtained in beautiful crystalline needles, whilst a black powder settles at the bottom of the tube. In this instance also pseudopurpurin is converted into purpurin.

The characters of purpurin are:—colour redder than that of alizarin; it sublimes at 250° C., but always with partial decomposition, leaving behind a carbonaceous residue. The crystals differ from those of alizarin, and commonly resemble the feather of a quill. When dissolved in boiling alcohol, they are re-deposited, on cooling, in crystalline needles, often r centim. in length, of a beautiful red, slightly verging upon orange. If dissolved in alcohol without previous sublimation, they form, on cooling, very small groups of minute acicular crystals. There is, however, no difference in their composition.

Purpurin is rather more soluble in boiling water and boiling alcohol than alizarin, but is otherwise soluble in the same liquids. Purpurin consists of C₁₄H₈O₅, or C₁₄H₅O₂(OH)₃. The carbon and hydrogen are given respectively at 66.67 and 3.70 per cent by Wolff and Strecker, but by Debus at 66.38 and 3.87, and by Schiffer and Schützenberger 65.93 and 3.29. Potassa, soda, and ammonia dissolve purpurin, yielding characteristic poppy-red solutions, quite distinct from the almost blue solutions yielded by alizarin under the same conditions. The presence of to per cent alizarin mixed with purpurin can be detected by solution in alkaline liquids, since the blue shade becomes distinctly perceptible on dilution with water. Alkaline carbonates and salts, which in solution exhibit a basic reaction, e.g., borax, dissolve purpurin, yielding red solutions. Alum water dissolves purpurin far more readily than alizarin, and the red solution does not, on cooling, deposit a sediment of purpurin, whilst alizarin is, in great measure, thrown down on cooling. The lakes containing both substances together yield purpurin when boiled with solution of carbonate of soda. The combinations of purpurin with bases have great similarity with the corresponding alizarin compounds. The alkaline purpurates are soluble in water; those of the alkaline earths and metallic oxides insoluble. The former are nearly black, yielding red solutions. Purpurate of soda can be obtained in crystals by a similar process to the alizarate. The alumina lake of purpurin is a full red, without the least trace of blue. The iron-lakes

are either violet or black. When hydrochloric acid is added to a recent solution of purpurin in ammonia, the colour is thrown down unaltered in the shape of orange-yellow flocks. If the solution has been kept even for twenty-four hours, the precipitate resulting from the addition of hydrochloric acid is a deep violet. The same result is obtained by heating the ammoniacal solution to 100° C. This precipitate gives off ammonia when heated with caustic soda, proving that an amide has been formed, purpuramide or purpureine. It is soluble in boiling alcohol, yielding a deep violet-red solution, and on evaporation forms crystals exhibiting a green reflection like those of murexide. This substance dyes wool and silk an amaranth shade without any mordant. Its formula is $C_{14}H_9NO_4$, or $C_{14}H_5NH_2(HO)_2O_2$. When a mixture of crystallised purpurate of soda, iodide of ethyl, and alcohol is heated in a sealed tube to 150° C., there is formed iodide of sodium, and a red crystalline substance sparingly soluble in alcohol. Its formula is $C_{14}H_5(C_2H_5O)_3O_2$.

Pseudopurpurin is almost insoluble in boiling alcohol, but soluble in hot benzol, from which it separates on cooling in fine acicular crystals of a brick-red colour. Heat, as well as treatment with alcohol at high temperatures in a sealed tube, convert pseudopurpurin into purpurin. Pseudopurpurin dissolves in alkalies with a red colour. With ammonia it forms an amido-derivative, in a similar manner to purpurin. The formula of pseudopurpurin is

C14H4(HO)4O2.

The orange matter is insoluble in boiling benzol; very soluble in luke-warm alcohol, from which it is deposited, on cooling, either as a thick granular curdy mass, or again as orange scales. This depends on the concentration of the solution. This substance is partially converted by the action of dry heat into purpurin. Its formula, according to Schützenberger, is $C_{20}H_{16}O_{9}$. Purpurin, pseudopurpurin, and the orange matter yield with mordants shades resembling those of alizarin, but without a blue reflection. Goods dyed with purpurin and the orange matter resist boiling soap-lye tolerably well, but the shades produced by pseudopurpurin fade away. The power to resist clearing varies, therefore, inversely as the amount of oxygen in the colour.

The yellow colour, purpuroxanthin, is soluble in alcohol and benzol, sparingly soluble in water, and sublimes when heated almost without decomposition. With aluminous mordants it yields a dull and fugitive yellow, which is destroyed by the per-salts of tin and by clearing. It is readily obtained by the reduction of purpurin, pseudopurpurin, or the orange matter, by heating to 180° C. in a sealed tube along with aqueous teriodide of phosphorus. It is more easily prepared by adding some protochloride of tin to a boiling solution of crude purpurin in caustic soda. The solution loses its red colour and becomes orange. The addition of an excess of hydrochloric acid throws down the yellow matter. It is then thrown on a filter, washed, and purified by sublimation and crystallisation from alcohol.

Turning now to the researches of Schunck on this subject, we may summarise his results as follows:—

a. By splitting up the rubian under the influence of boiling dilute hydrochloric or sulphuric acid he obtains—(1) alizarin; (2) rubianin, a lemonyellow matter, crystallisable, and more soluble in water, but less so in alcohol

than alizarin, and yielding, on elementary analysis, carbon 57:42, hydrogen 5:30, the rest being oxgen. These figures may be formulated—

 $C_{20}H_{20}O_{10} = C_{20}H_{12}O_6 + 4H_2O$, or $C_{20}H_{22}O_{10} = C_{20}H_{12}O_6 + H_2 + 4H_2O$. There is little doubt but that rubianin may exist pre-formed in madder; (3) rubiretin, or a resin, a brown-coloured fusible substance; formula—

 $C_{20}H_{16}O_6 = C_{20}H_{12}O_6 + H_4$.

b. By the action of boiling solutions of caustic alkalies rubian yields—(1) alizarin; (2) the resins α and β described above; (3) a yellow matter obtained in crystals from an alcoholic solution, and capable of subliming. It is soluble in water, and has been named rubiadin. It contains—

Carbon	 	 	 	71.22
Hydrogen	 	 	 	4.83
Oxygen	 	 	 	23.95
			-	
				100.00

By splitting up rubian with a peculiar ferment (erythrozym) contained in madder it yields—(r) alizarin; (2) resins α and β ; (3) rubiafin, a yellow, crystalline sublimable matter, composed of—

Carbon	 	 	 	69.30
Hydrogen	 	 	 	4.26
Oxygen	 	 	 	26.14
				00.001

(4) rubiagin, a yellow matter, crystallising in small needles, and yielding-

Rubiadin and rubiafin appear to be one and the same substance, representable as $C_{20}H_{16}O_6$. Rubiacin, or madder-orange, first discovered by Runge, may be obtained in brilliant flakes and masses, or in the shape of needles of a yellow colour, resembling in shade fodide of lead. This substance is sublimable unchanged, and is sparingly soluble in boiling water, but readily soluble in boiling alcohol. It contains—

Rubiacin dissolves in sulphuric acid, yielding a yellow solution, unaffected by heat. It is decomposed by boiling sulphuric acid. If rubiacin is dissolved in perchloride or pernitrate of iron, a brownish-red solution is formed, which turns yellow on the addition of acids, and deposits rubiacic acid as a flocculent mass. This dissolves in alkalies, giving purple solutions, from which acids re-precipitate the rubiacic acid unchanged. The ammoniacal solution gives a dirty red precipitate with chlorides of barium and calcium. If hydrate of alumina is added to an alcoholic solution of rubiacin it takes an orange colour, whilst the liquid is rendered colourless. This aluminous lake is soluble in caustic potassa, yielding a purple solution, a particular in which

this compound differs from the corresponding alizarin lake. Mordanted cloth scarcely takes any colour if immersed in a boiling rubiacin bath. Rubiacic acid is re-converted into rubiacin by the action of sulphuretted hydrogen. In many of its properties rubiacin approaches purpuroxanthin as obtained by the reduction of purpurin. According to Schunck, rubiafin, when acted upon by the per-salts of iron, yields rubiacin. Since rubiafin = $C_{20}H_{16}O_6$, it will lose by oxidation 4 atoms of hydrogen, becoming $C_{20}H_{12}O_6$.

The following is a summary conspectus of the colours of madder:-

Original Colours Soluble in Water.

Glucosides, which by the action of acids, alkalies, and ferments are split up into sugar and colours insoluble in water:

Rubian (Schunck). Amorphous, bitter, very soluble, precipitable by porous substances. A mixture of several glucosides.

Ruberythric Acid (Rochleder). Crystallisable, alizaric glucoside, convertible only into alizarin and sugar.

Colouring Matters, the Existence of which cannot be Doubted.

Insoluble colouring matters due to the splitting up of the glucosides, and present in the ground madder of commerce.

- r. Alizarin. Readily sublimable without decomposition, orange-red, crystallises in needles; yields in dyeing and printing very fast and beautiful colours, which resist the clearing operations.
- 2. Purpurin. Sublimable with partial decomposition; red, crystallises in needles; yields in dyeing shades not quite fast, but which stand clearing moderately.
- 3. Orange Matter. Crystallises in granular scales, very soluble in alcohol; yields on sublimation purpurin, but leaves a large deposit of carbonaceous matter. Behaves like purpurin in dyeing.
- 4. Pseudopurpurin. Brick-red; insoluble in alcohol, soluble in boiling benzol, and deposited, on cooling, in crystalline needles; decomposed by heat, yielding a very small sublimate of purpurin. Gives with mordanted cloth the same shades as purpurin, but none of these stand clearing.
- 5. Purpuroxanthin, or xanthopurpurin. Yellow, crystalline, sublimable, formed by the reduction of purpurin.

Colouring Matters of Doubtful Existence, or which Require Further Investigation.

Yellow matters.—Rubianin, rubialin, rubiazin, rubiadin, rubiacin, rubiacic acid.

Resinous matters .- Verantin and rubiretin.

Commercial Products or Derivatives from Madder.

The madder of commerce yields, when properly treated, beautiful and exceedingly fast colours with alumina and iron mordants. Care must be taken to submit the dyed fabric afterwards to a series of operations known as clearing (avivage). But madder is in many respects inconvenient as a dye, this defect being chiefly, if not entirely, due to the presence of foreign substances along with the colouring principles. When the previously mordanted or printed fabrics leave the dye-beck, the red, rose, and violet

shades produced by the various mordants are dull and unsightly, because the mordants fix not merely the alizarin and purpurin, but also the yellow and brown colouring matters. Further, those portions of the fabric intended to remain white, become dirty, because these last-named matters adhere to such parts. In order to utilise all the disposable colouring matter present in the madder, it is requisite to raise the temperature of the bath gradually to the boiling-point. Without this precaution a serious loss would ensue. In addition to these disadvantages of madder, which refer especially to printing calico and silk, not to dyeing wool a uniform colour, it is not possible to utilise all the colouring matters contained in the root. Nearly half the colouring matter is combined with lime-salts and with woody fibre so intimately that it cannot be united with the mordants of the fabric. In consequence the spent dye-material still contains alizarin, which can be utilised, as we shall show below in treating of garanceux. Since the beginning of this century many proposals and attempts have been made to obtain the colouring principles contained in madder in a higher state of purity and concentration. Up to this day no one has succeeded in entirely eliminating the useless constituents present in madder in one operation. The dyers and printers, moreover, exercise great caution in adopting in place of madder preparations about which they can often judge only by somewhat prolonged use. Garancin had to struggle for years against the scepticism of the trade before its use became general.

In the following pages we propose to classify the commercial preparations of madder according to the kind of treatment to which the madder is subjected in their preparation:—

r. Processes which increase and concentrate the tinctorial power of the madder by the elimination of foreign substances soluble in water, or capable of being rendered soluble by means which do not modify the colouring matter.

2. Processes whereby the solubility of the colouring matters in certain menstrua is utilised to separate them from materials insoluble in the same.

3. Processes based upon the volatility of the colouring matters.

4. Treatment purely mechanical.

The reader should bear in mind that the tinctorial matters of madder form three groups—the glucosides soluble in water; the colouring matters free but mechanically mixed with other vegetable matter; colours intimately combined with woody fibre. The heart of the root, a very hard tough woody mass, contains a large amount of excellent colour. The heart of the Zealand root may be readily obtained, and after having been separately ground, yields pure alizarin on being sublimed with care in small portions.

First Group .-

Fleur de garance, or flowers of madder, of Julian and Roquer, of Avignon. This preparation should not be confounded with the older preparation of Robiquet, Colin, and Lagier of the same town, which is now known as garancin. As far back as 1823, Kuhlmann came to the conclusion that washing madder in cold water would be an easy method of removing gum, sugar, and certain extractive and yellow colours, such as xanthin. When madder, thoroughly moistened with water, is left to stand previous to being washed, a fermentation of a peculiar character ensues, which splits up the glucosides, and increases the tinctorial power to some extent.

In 1846 and 1847 Roux patented the application of fermentation to madder to obtain thereby a peculiar preparation. This process was found very capricious, since the temperature, the duration of the steeping, the quantity, and also the quality of the water so much affect the results that a slight change in any of these particulars is enough to render the madder useless.

Julian and Roquer describe their own process thus :-- We take madder roots and reduce these to powder; the madder thus obtained is placed in tanks, and, after the addition of water, is thoroughly and vigorously stirred up with that water, which we take cold or hot, and which we treat according to its degree of purity with any acid to eliminate its contained lime-salts. We then run the entire contents of the tanks into the filtering boxes, consisting of stout wooden frames, lined with flannel; the bulk of the liquid is suffered to run off, and, according to the product we desire to obtain, we leave the madder in these boxes for a length of time, varying one to five or six days, according as it suits our purpose to produce alcoholic fermentation or not. The madder is taken from these boxes and put into stout linen bags, and strongly pressed by means of hydraulic presses of great power; the pressed cakes are dried in stoves (heated by steam, and arranged similar to those of the sugar refineries), ground up to powder, and packed into casks. The liquids are either collected for fermentation or run off into the sewers; if fermented by the addition sometimes of beer yeast, but chiefly by means of sufficient fermentationinducing nitrogenous matter present in the liquors naturally, we submit the latter to distillation and obtain alcohol. The first samples of their product were sent in January, 1851, on trial to Mulhouse, and in February, 1852, Messrs. Julian and Roquer had sent off from their works at Avignon 300,000 kilos. of fleur de garance. By the process described the madder loses half of its weight of useless materials.

M. Pernod, of Avignon, has kindly given the writer the following information on the more recent mode of preparing bloom of madder:-The madder is mixed with from eight to ten times its weight of river water (the less saline matter present the better), to which just so much sulphuric or hydrochloric acid is added as will saturate the carbonate of lime always present in the pulverised madder. When sulphuric acid is employed, from 1 to 2 kilos. of the concentrated acid are applied for every 100 kilos. of madder; the addition of the acid is chiefly made when it is intended to prepare a material particularly suitable for the dyeing of red and brown colours, but when the preparation of a material especially suited for violet dyeing is desired, no acid at all is used: this operation is done in a wooden tank, lined inside with stout flannel, which rests on a false perforated bottom, between which and the real bottom a small space is left provided with one or more taps, so placed as to ensure the running off the liquid when desired, while the pasty mass remains on the filter supported by the false bottom. The madder is left macerating in the liquid for about twelve or fifteen hours, when it is tapped off; and since this has taken up the largest portion of the sugar present in the madder, it is run into tubs of suitable size and construction, and left to ferment, to be converted into alcohol by distillation. The pasty material which remains inside the tank is immediately taken out and placed in stout linen bags, in quantities of from 3 to 4 kilos., and submitted to very strong pressure by means of the hydraulic press, in order to remove the largest portion of the liquid; after which the material is removed from the bags. It is transported to the drying-stove, and after having become quite dry it is reduced to powder by mill-stones similar to those used for the grinding of madder. This millwork is very different from that used for grinding grain, and more resembles that in use for grinding coprolites. The ground-up material is packed in casks, commonly lined with stout paper inside, while the seams between the staves are covered with pitch.

Bloom of madder is also prepared by mixing the madder with from eight to ten times its weight of river water, and leaving this mixture for from two to four days at rest, at a temperature of from 18° to 25°. When the alcoholic fermentation which sets in is complete the liquid is run off, and the operation is finished as just mentioned. When the alcoholic fermentation takes place in the presence of a large quantity of water, the colouring principles of the madder do not suffer any change, and are not decreased in their tinctorial value; but when either the pasty mass-above referred to as left in the filter tank—or the pressed cake is suffered to undergo fermentation, the colouring principles are sometimes altered and somewhat deteriorated, and on that account, and in consequence of the irregularity of the fermenting process under these conditions, it is no longer used in the Avignon district. 100 kilos. of madder yield from 55 to 60 kilos. of bloom of madder, according to the nature of the raw material. Generally speaking, the better qualities of madder yield a less weight than the lower qualities, but the tinctorial value is very superior. The quantity of madder annually converted into bloom of madder in the Avignon district amounts to 4,000,000 kilos.

The manufacture of alcohol from madder is a profitable business: 100 kilos. of madder yield from 7 to 10 litres of alcohol, at 87 per cent; the superior kinds of madder yield a larger quantity than the lower. This alcohol, in the raw state, is unfit for drinking. Its taste is very disagreeable, and its smell much like that of wood-spirit. It is employed for the preparation of varnish and ether. M. Schützenberger states, probably upon the authority of some of the distillers resident in the Avignon district (it should be mentioned that some of the manufacturers of fleur de garance are distillers at the same time, but many sell the fermented or fermentable liquid, or raw spirit, to distillers), that the alcohol from madder can be rendered quite sweet by contact with porous substances—especially pumice-stone and wood-charcoal—and re-distillation, and then become as good as rectified beet-root alcohol. There is established at Sorgue, near Avignon, an extensive distillery, wherein the largest portion of the alcohol obtained in that district is rectified and purified to such an extent as to compete successfully with the alcohol obtained from wine. According to the opinion of some chemists * the peculiar odour and taste of the alcohol

^{*} The researches of Gunning, of Amsterdam, have proved that the odour of the alcohol obtained from the washing-liquors of garancin and fleur de garance is due (in the case, at least, of Zealand madder) to acetic ether and aldehyde. The raw madder-spirit is an exceilent source for aldehyde-ammonia. The preparation is as follows:—From 20 to 30 litres of the impure spirit are placed in a still provided with a long copper worm, and heated to 60° or 70° C., while at the same time a rapid current of air or carbonic acid is passed over the liquid. The distillation is continued until the distillate ceases to give a darkish colouration with caustic potash-lye. To the distillate is added twice its bulk of water, powdered hydrate of baryta being stirred in till a decided alkaline reaction is perceived, in order to decompose the acetic ether. The excess of baryta is removed with carbonic acid. Aldehyde is afterwards

obtained from madder is due to amylic and other homologous alcohols, and partly to the existence of a peculiar camphor-like substance present in madder, and known as camphor of madder. This substance, according to the researches of M. Jean Jean, is isomeric with the Borneo camphor (C₁₀H₁₈O). The camphor from madder can be obtained in small hexagonal prismatic crystals; it is hardly soluble in water, readily so in acetic acid, alcohol, and ether, and turns the plane of polarisation to the left. The great advantage of fleur de garance, or rather its superiority to madder, especially for printing, is owing to the purity and great beauty of the violet tints produced by this material, with equal fastness but superior brilliance. The simple reason is, that by the operation to which madder is subjected, to produce bloom of madder, all the soluble, mucilaginous, saccharine, and brownish-coloured matters are removed from that substance; and since these substances interfere with iron mordants, and thereby deteriorate the violets, it is clear that flowers or bloom of madder yield a superior violet.

With alumina and iron mordants bloom of madder produces deeper shades than madder. This seems to be due to the solvent action exercised upon the mordants by the substances soluble in water present in madder; and the degree of this action may be judged from the fact that when bloom of madder is used the same intensity of colour is produced as with madder, with mordants of from fifteen to twenty times less strength than madder would require. The rose-red and red shades produced by fleur de garance are quite as beautiful as those which madder gives, and have, as compared with madder, the advantage of greater fastness. The portions of the fabric intended to remain white are less soiled when bloom of madder is used than is the case when madder is employed. There is an advantage gained, also, in respect of clearing and soaping. The other advantages of bloom of madder aregreater regularity of dyeing; less difficulty in the management of the dyebath; the possibility of adding a fresh portion of bloom to the bath when it appears exhausted, which cannot be done when crude madder is used; and the perfect exhaustion of all colouring matter from the bath. It should be understood, however, that what is here said relates exclusively to calicoprinting,-that is to say, to the passing of calicoes, muslins, and such-like fabrics, upon which designs have been printed by rollers supplied with the requisite mordants, through the dye-baths. Bloom of madder is not used in dyeing woollen fabrics to which a uniform shade is to be given, neither for Turkey-red. Bloom of madder is preferable, since for equal weights it contains twice as much colouring matter as madder, and it has the decided advantage that it is less sensitive to damp warehouses, and does not, like madder, become spoiled by age.

The length of time madder can be kept and preserve its full vigour differs for different kinds of madder. Counting from the moment the ground material is packed in casks, Avignon madder and the produce of Southern Europe

separated from the liquid by careful distillation in the water-bath, and purified by combination with ammonia. If the impure madder-spirit is agitated with sodium amalgam, perfectly pure alcohol is obtained, since the aldehyde is thus hydrogenised to alcohol, the acetic ether being also decomposed with formation of alcohol and acetate of soda. The opinion has been entertained that there is a relation between the amount of sugar present in madder and the amount of the tinctorial principles.

and the Levant are in full perfection before the end of a twelvemonth. Alsace, Baden, and Wurtemburg madders are perfect in about sixteen to nineteen months. Zealand madder reaches its climax, for all shades, at from twenty to twenty-six months. This is the unanimous testimony of Mulhouse, Rouen, Elberfeld, and other places where this material is consumed, and is supported by Gasparin, Girardin, Prévinaire, and other scientific men, that no known kind of madder produces then such fast, such brilliant, and such intense colours as that of Zealand. There is the drawback of clearings, and, as regards the white portions of tissues, almost an impossibility of brightening them without grass-bleaching. The other kinds of madder are entirely spoiled, even within a few weeks after having reached maturity. Zealand madder, if properly kept, is-even at thirty-six months of age—quite fit to dye excellent deep browns and exceedingly beautiful blacks. Gasparin accounts for this by the mode of cultivation to a great extent, and by the peculiarities of the soil. The proper packing of the material and the care of warehousing it in suitably constructed and ventilated-yet dark*buildings have been proved to have much to do with the good qualities of Zealand madder, by the experience of the brokers and warehousemen who have charge of this article at Rotterdam. There higher rents are readily paid for warehouses suitably constructed to keep madder. An equable temperature is also a great point.

We now return to fleur de garance: from its mode of preparation we may already infer that, as is the case with madder, the colouring matter intimately combined with and pre-existing in the woody fibre is lost. According to M. H. Schlumberger, 100 parts of fleurs de garance are equal to 200 of madder, but the loss of colouring matter just alluded to is the same for both, and amounts to about 45 per cent. Hence for bloom of madder, as well as for raw madder, there exists the necessity of treating the residues for garanceux, about which we shall treat presently.

We have now to treat of *Garancin* (once known as Lagier's bloom of madder). The principle of the manufacture of garancin is based upon the action which sulphuric acid, in a more or less concentrated state, has upon madder, whether previously washed or unwashed with water. The action of the acid destroys a portion of the woody fibre, and while it does not affect the genuine colouring principles it removes the useless vegetable matter, dissolves the calcareous and other combinations of the colouring substances, and sets so much of the latter entirely free that a real gain is obtained, so great as to cover far more than the expense of the acid and the manipulations required.

As far back as the year 1828 Robiquet and Colin wrote a paper, presented to the Société Industrielle de Mulhouse, "On the Concentration of Madder by Means of Sulphuric Acid." These chemists proposed to treat Avignon madder with a quantity of concentrated sulphuric acid equal to its own weight, or even somewhat more. They thus obtain what they call charbon sulfurique, rich in colouring matter, and fit for dyeing purposes after washing out the acid. This substance, however, has never been manufactured on the large scale, nor

^{*} While direct sunlight is carefully avoided, even daylight is hardly admitted in these places, and a too great damp, as well as too great heat, are considered injurious, but extreme cold is equally avoided. Care is taken now and then to move the casks, i.e., roll them about thoroughly.

has it ever served the use of dyeing. All that has ever been done with the comparatively small quantity made has been its extraction, either with alcohol or a boiling solution of alum, to prepare what has been called the colorin of Messrs. Lagier and Thomas. M. Henri Schlümberger has, however, tried dyeing with this charbon sulfurique, and found that it gave the red, violet, and black tints perfectly well, while the white portions of the tissue were almost unsoiled. No action ensued until the boiling-point of the liquid in the dyebeck was nearly reached.

In 1828, Lagier, Robiquet, and Colin took out a patent, from the text of which it is quite clear that they intended to produce from madder a more easily manageable suustance by means of sulphuric acid. They proposed (and actually carried out) a preliminary washing of the madder with water, in order to remove from it all soluble matter. In consequence, the quantity of sulphuric acid was decreased, since, by the previous washing out of a portion of the sugar, that substance no longer neutralised the effect of the acid, although the addition of the concentrated acid to a thoroughly moist mass would, of course, cause its dilution to some extent. More water was added to the acid previous to its addition to the washed and moist madder, which immediately after was heated, by means of steam, to 100°. This is, briefly related, the original method of making garancin. This substance has

only very gradually come into use.

At present garancin is made as follows:—Madder is mixed with from eight to ten times its weight of water, acidulated with sulphuric or hydrochloric acid; from 1 to 2 kilos. of acid for every 100 kilos. of powdered madder being a sufficient quantity. As regards the acids, it is essential that the sulphuric acid should be, as far as possible, free from nitric acid or nitrous compounds, and should not contain metallic substances in solution. The hydrochloric acid ought not to contain any free chlorine, and should be also free from metallic compounds. These particulars are too often overlooked, yet experience, especially in Holland, has proved that the goodness of the acids influences the goodness of the garancin produced. This washing process is executed in large wooden tanks, fitted with a stout flannel lining, resting upon a false or perforated bottom, as already described for the preparation of fleur de garance.

In the case of garancin the madder is left steeping in the acidulated water for about seven to twelve hours, after which the liquid is run off. This fluid also serves for the manufacture of alcohol. The mass in the tank is transferred to another wooden tank, and sufficient water is added to make a thin paste of the whole, to which there is then added—for every 100 kilos. of madder originally taken—30 kilos. of strong sulphuric acid or 40 kilos. of strong hydrochloric acid. After this mixture has been well stirred up the cover of the tank is closed, and, by means of a lead pipe, steam is introduced into the magma, which is kept boiling for three or four hours. When ebullition has been kept up for that time, the contents of the tank—while yet hot—are brought over into a very large tank, lined with flannel and provided with a perforated false bottom, This tank is partly filled with cold water, the purer the better, the water having a decided influence upon the goodness of the resulting garancin. After all the material is transferred from the boiling tank into the filtering basin, the water contained is run off and fresh water added,

and the washing repeated three to five times. The last washings assume a colour not unlike red Hermitage wine.* When the liquid has run off as far as possible the garancin is farther dried, first by being pressed—in powerful hydraulic presses—into cakes, which, after having been stove-dried, are broken up and reduced to powder by a mill.

The washings from garancin—especially the first, which contains most of the acid—are applied in various ways, either for washing illuminating gas, and removing ammonia therefrom, or for dissolving phosphatic minerals for the manufacture of artificial manures and the like; the subsequent washings contain, according to recent reports,† a peculiar pigment, and also oxalic acid.

One hundred kilos. of madder produce from 34 to 37 kilos. of garancin, according to the quality of the madder employed. The superior qualities yield a smaller quantity of garancin than the inferior. When madder which has not been previously washed is acted upon by acid, as just described, the result is a very dark—almost carbonised—material. This colouration is due to the decomposition of the chlorogenin, which is converted into chlorrubin.

There are several points connected with the manufacture of garancin which are scarcely or not at all explained by Science, and, moreover, its preparation from Zealand madders especially requires far more careful study and attention than is the case with Avignon or other madders grown in Southern Europe. What is the real and essential action of the acids in producing garancin is not known. It has been thought that they acted by breaking up the woody fibre, tearing it asunder, and letting the water get access to the colouring particles previously enclosed, and so transferring them to the dye-bath; but the weakness of the acids which can be employed, consistent with successful issue, is fatal to this explanation. The supposition that the colouring matter is in a state of combination with some earthy base, as lime and magnesia, and that it cannot dye while so combined, and that the acids liberate the colouring matter by combining with the bases, is an explanation not supported by any real facts or experiments. It appears probable that some chemical affinities of a more refined and subtle nature are brought into play. It is likely that the acid employed forms a combination with the colouring matter, which is itself easily decomposed even by water. It is not in accordance with analogy to suppose any formation or creation of colouring matter, but simply that a portion of the colouring matter is present in some form or other upon which water cannot act, whilst acids in some unknown manner make it susceptible to the influence of water. There are some ascertained facts bearing upon the action of acids upon the colouring matter of madder, which, though they have no direct practical significance, are full of suggestions. It is very well known that garancin is not the same as a dyeing material as madder. Its colours are not so fast, either as against soaping, clearing, or exposure to air; the acid having evidently, if not injured, at least somewhat altered, the colouring matter in setting it free. It is no longer what it was in the untouched root. Chemistry has hitherto failed to explain this, which, as a fact, stands in opposition or exception to other known cases of the action of acids upon the colouring matter of this root. For example, a piece of Turkey red cloth or dark purple dyed with madder can be treated with strong sulphuric acid, which

^{*} Genuine Hermitage rouge has a delicate yellowish rose-red shade.

[†] See "Chemical News," vol. xxi., p. 58, February 4, 1870.

will take up the mordant, and leave the colouring matter loosely attached to the cloth. The acid can be removed by washing, and then the colour extracted by spirits of wine. This colouring matter may have been subjected to the contact of acid quite as strong as that used in making garancin (and even far stronger), and for as great a length of time, but it is not affected like the colouring matters in garancin. It can still dye up fast reds, pinks, and purples, upon mordanted cloth; yielding colours which are not injured, but improved, by soaping and clearing. The question arises, Why should acids act so differently in one case and in the other? It can be easily understood how great an advantage it would be if garancin gave as fast colours as madder. This result may perhaps be accomplished when we have a more accurate knowledge of the action of acids upon madder.

In the beginning of 1870 a brief private communication was received by us from the chemist in charge of the four largest garancin works in Holland. The manufacture of garancin from Zealand madder, made by the old-fashioned plan, is attended with some practical difficulties, to remove which the aid of science has been called in. Researches have been made—not only by the chemist just mentioned, but also by Prof. Mulder, of Utrecht, and others—which show that the garancin so prepared is as good for all practical purposes as the best madder, and the colours are equally fast, while the dyeing operations are easier and take less time in clearing; the process, however, is kept a trade secret. We are informed that this garancin also dyes Turkey red rapidly.

The Avignon garancin usually met with in commerce is a finely pulverised powder, of a more or less deep brown colour. The ligneous matter is not at all carbonised, as can be proved by exhausting the substance successively with soda and acid, when a residue is obtained free from colouring matters, hardly any deeper in colour than fleur de garance. 100 grms. of garancin yielded from 16 to 17 grms. of pectic acid, the greater part of which is in a free state, while a small portion is combined with lime. At the same time 48 grms. of ligneous matter (woody fibre) is obtained. Since 100 grms. of madder (Avignon) containing 20 of ligneous matter yield about 40 grms. of garancin, it is clear that the woody fibre is very little acted upon by the treatment with sulphuric acid.

The tinctorial value of garancin of good quality is from 4 to 4'5—even sometimes 5—times greater than that of the madder it is obtained from; too parts of madder, by weight, yield from 36 to 40 parts of garancin.

While garancin has its decided advantage, especially as regards the great saving of time, expense, and labour in the production of coloured designs for printing, it cannot be used as a substitute for madder. Garancin colours are less fast and solid than those from madder with the same mordants, and some of the shades are always decidedly inferior to madder shades of the same kind. It has been proposed to remedy this defect by the addition of a small quantity of chalk to the garancin bath, but this remedy is attended with a real loss of what was gained by the previous treatment of the dye-stuff with acid. The generally prevailing opinion on this practical inconvenience is, that it is due to the presence of a small quantity of ligno-sulphuric acid* which is intimately

^{*} There have been numerous proposals made, and a large number of Patents have been taken out, to remove from garancin all the sulphuric acid, but the application of alkalies—even in the

combined with the material, and not removable by washing with water alone. The experiments made by Schwartz with oily extracts from garancin yielded shades as fast and beautiful as those from flowers of madder, while the addition of the ligneous matter from garancin was alone sufficient to impair these characters.

Some manufacturers add to the garancin, after having been stove-dried and while being ground up, a small quantity of bicarbonate of soda or precipitated chalk, well washed and dried, in order to absorb the acid. It has also been proposed to improve garancin by exposure to the vapours of ammonia, and to dry the material afterwards by steam.

Garanceux.

The manufacture of garanceux from spent madder is essentially the same as that of garancin, and the same general explanations apply equally to either. The method of making garanceux is simple and well understood, and requires nothing but care and attention to yield regular results. The spent madder from the dye-beck and wince pits is collected in a sufficiently large pit and allowed to settle, usually with the addition of weak sulphuric acid, which both stops any inclination to fermentation and throws down a fine powder which otherwise floats in the liquor. The wet mass should be well pressed, until it does not contain more than two-thirds of its weight of water. Instead of a press, the centrifugal hydro-extractor-as used in sugar-refineries-is often used, with the advantage that it is not needful to break the matter up afteryards. The quantity to be used of the acid may vary, but a dozen pounds of brown acid (chamber acid) is a good proportion to the hundredweight of spent madder. The acid should be mixed, before being added to the madder, with about 3 gallons of water. It is essential that the acid touch all the particles of madder, and therefore the material should be thoroughly worked through; after which the mass may be left for days, or even weeks, before it is steamed. The operation of steaming must be watched, to see that all the madder gets a fair proportion of steam. If the spent madder be too moist it sets in the steaming cisterns, and forms chinks, through which the steam blows without permeating the whole mass. It should be so moist as to yield water upon pressure between the fingers, but not wet enough to stick together when pressed in the hand. The thorough washing of the garanceux is of course important, but it has the advantage of washing much faster and more easily than garancin, on account of its loose structure. The washing is known to be accomplished by the liquor no longer tasting acid, and by the appearance of a fine slimy powder, which never shows till the washing is almost completed. It is not advisable to use any alkali to neutralise the remainder of the acid, but it is sometimes done, and then crystals of soda or milk of lime may be added in proper quantity. It keeps better if left a little acid, and can be neutralised in the dye-beck with safety. When the washing is complete it should be pressed again.

Well pressed garanceux contains between a third and a fourth of its weight of dry matter, the remainder being water. Its tinctorial value, in proportion to garancin of the first quality, will vary according to the nature of the madder,

state of bicarbonates and of ammonia gas—has (unless very carefully applied and skilfully managed) the effect of injuring the garancin. Many years ago Drs. van Vlaanderey and Baumhauer proved garancin to contain ligno-sulphuric acid.

and to the proportion in which it has been spent in the first dyeing. Garanceux from mixed Turkey (Levant) and French madder is equal, as it comes from the press, to from one-sixth to one-ninth of its weight of really good garancin. When dried it is equal to about one-third. It is of the utmost importance to see that the garanceux is properly neutralised either in the dye-beck or before it goes in. An error on either side, that is to say, an insufficient or an excessive quantity of alkali, is equally injurious. The most useful matter for neutralising garanceux in the becks is bicarbonate of soda, which is very regular and mild in its action. The proportion to be used depends, of course, upon the degree of acidity; the highest amount required is about I lb. of soda to 70 lbs. of garanceux. If the acidity passes this limit good results will not be obtained, and the garanceux should be washed over again. The lowest amount of soda required will be about 1 lb. to 100 or 150 of garanceux taken in the wet state." The injurious effects of too much soda are perhaps even more marked than a slight deficiency. The colours are dull and cloudy without brilliancy or solidity. A deficient quantity of soda is shown by a redness of the chocolate colours, poorness in the blacks, and general bareness of the whole of the colours. The colours which garancin and garanceux yield with properly mordanted cloth are the same as those from madder; the whites are purer, on account of the absence of the soluble matters which stain them in madder dyeing. The colours will not stand a severe soaping, and cannot be brought to the same degree of brightness as those produced from madder. These products are not much employed alone, but generally in combination with some of the cheaper dye woods.

Commercial alizarin or pincoffin has been sold by M. Pincoffs, of Manchester, since 1854. This material is remarkable for the beautiful lilacs or violets it yields without soaping. It also admits of producing combinations of lilacs with catechu, lilac and chocolate, and lilac and orange, which results cannot be obtained satisfactorily with madder or garancin. This material, further, economises the mordants, and produces

lilac shades, which may be graduated ad libitum as to cost.

Pincoffin is prepared by submitting garancin of good quality, and as neutral as possible, to the action of dry or superheated steam. It may also be obtained by heating garancin or fleur de garance to 200° C. on an oil or sand-bath. It is very probable that the chief result of this operation is the destruction of the fawn-coloured resinous matter which is associated with alizarin. Hence the colour cannot foul the purples or lilacs by its action upon the iron mordants. When fleur de garance, dried at 100°, is acted upon by fluoride of boron a carbonaceous matter is obtained, which, after washing with water, yields, on being heated with alcohol, a colouring matter dyeing lilacs and purples as well and as beautiful as the commercial alizarin. The tinctorial value of the commercial alizarin is rather lower than that of garancin. Some authorities state that about from one-sixth to one-fourth more of this material is required for the saturation of an equal weight of mordant for lilac.

Mr. Higgin has devised another method of preparing commercial alizarin. He boils garancin with some carbonate of soda or a little ammonia. The liquid, which is alkaline at starting, becomes acid after boiling for twenty-four hours, when the garancin is converted into alizarin.

M. E. Schwartz has proposed to substitute for garancin a preparation obtained by mixing gradually in the cold fleur de garance with from four to

five times its weight of sulphuric acid of sp. gr. 1.714, or 143° Tw. By this operation a portion of the ligneous and pectic matters become so disintegrated as to be soluble in water. The magma of fleur de garance and acid is therefore poured into a very large bulk of water, when a sediment is thrown down, which, after having been thoroughly washed, dried, and pulverised, becomes a fine brick-red powder, known in commerce as "carmine-madder." This material has a tinctorial value exceeding that of madder by seven or eight times. Owing to practical difficulties, and the expense of production on the large scale, this substance has never been manufactured to any extent. It yielded, when tried on the small scale, exceedingly good results in dyeing.

Second Group .-

Mechanical Process of Purifying Madder.—M. Pernod has tried to wash the previously coarsely ground madder root upon a metallic wire gauze sieve under a current of water, whereby the colouring matter is carried off, while there remains on the sieve a greyish-looking, woody, fibrous material not containing any more colouring substances. The pigment washed out is allowed time to settle under water. The water is run off, and the substance is placed on filters and dried. The brown powder thus obtained has a tinctorial value seven or eight times greater than that of flowers of madder, yet it contains, as might be expected, a large quantity of foreign matter.

The processes based upon the solution and consequent extraction of the colouring matter of madder are very many; indeed we may say that nearly all the solvents capable of taking up the colouring matters from madder have been tried to produce what may be in a general way called extracts of madder. Many of these materials have a high tinctorial value, exceeding from twenty to seventy times that of the same weight of madder. These substances are sometimes named after the vehicle employed for extraction. Thus we have the alcoholic, methylic, glyceric, and acetic extracts, to which names are usually added those of the inventors. These substances contain in general the colouring matters more or less contaminated with resinous and extractive matter. When these madder derivatives are treated repeatedly with a boiling solution of alum the resinous matter is left, while the colouring principles are dissolved. The same result is obtained when these extracts are exhausted with water heated under pressure to 250°. As far as these substance have been actually employed, they have answered well in dyeing printed fabrics, especially if chalk is added. The bath requires almost a boiling heat, and, in order to exhaust the colouring matter, it is best to rub the dry extract up with alcohol, and to use far less water in the beck than with raw madder. When madder and flowers of madder are acted upon by any neutral solvent, e.g., alcohol, wood-spirit, sulphide of carbon, glycerin, or by mild alkaline solvents, as carbonate of soda, phosphate, pyrophosphate of soda, weak caustic soda, or any alkaline borate, silicate, or oleate, that portion only of colouring matter is extracted which exists in a free state, while the portion intimately combined with the ligneous matter is left untouched. A complete exhaustion of the colouring matter can only be effected by the aid of mineral acids, which disintegrate the woody fibre and decompose the calcareous combination of the colouring matters. Hence it is clear that the preparation of the above extracts can be only suitably performed with either fleur de garance or garancin, or with charbon sulfurique.

We will now rapidly review the methods which have been employed for

obtaining extracts of madder :-

r. Messrs. Robiquet and Colin exhaust their charbon sulfurique either by means of a boiling solution of alum, and precipitate the colouring matter with sulphuric acid; or they employ alcohol first, cold, to wash out a resinous greasy matter, and a deep red-brown liquid not applied for any useful purpose, though the alcohol is recovered. The charbon sulfurique is next exhausted with boiling alcohol in a suitable apparatus. In this manner a very concentrated tincture is obtained, from which the colouring principles are abstracted by the addition of water. The precipitate is separated by filtration, and after having been pressed to remove moisture, is sold under the name of "Colorin." The tinctorial value of this substance is equal to seventy times its weight of madder, a result especially due to the treatment with cold alcohol, whereby the greater part of the resinous matter has been got rid. Garancin as now made can be treated in the same way, yielding the same results.

2. M. Kuhlmann treats madder with boiling alcohol, evaporates to the consistence of an extract, which he washes with water to remove the substances soluble therein. This process is faulty, as it is impossible thus to extract all

the useful matter from the ground root.

3. MM. Persoz and Gaultier de Claubry exhaust madder—first, with a boiling solution of carbonate of soda, and next, with an alum solution heated up to 100°. The sodic solution yields, on saturation with an acid (chlorhydric), a gelatinous precipitate of pectic acid mixed with colouring matter. This precipitate may be treated with alcohol, which leaves pectic acid and takes up the pigments.

4. M. Dandrillon steeps madder in hydrochloric acid, and treats next with boiling alcohol. The filtered liquid is saturated with chalk, concentrated,

and precipitated by means of water.

5. M. Colomb steeps madder in dilute nitric acid, and washes the acid out after some hours. The madder is next submitted to the action of caustic soda lye (sp. gr. 1.094 = 18° Tw.). The violet-coloured alkaline solution is precipitated with dilute nitric acid, and the ensuing bulky precipitate is well washed and treated with boiling alum, whereby the colouring matter is taken up and reprecipitated by means of any acid. The solution may also be precipitated by means of carbonate of soda, yielding a madder lake.

6. According to M. E. Schwartz, a large portion of the colouring matter of madder may be readily extracted from either garancin or fleur de garance by hot poppy or any other boiling oil. On cooling these oils deposit an extract,

which yields brilliant, fast, and resisting colours.

7. MM. Gerber and Dollfus exhaust fleur de garance with boiling woodspirit. The concentrated liquors are precipitated with water, yielding 63 per cent of a yellowish-brown extract. The residue of the raw material is acted upon by a fresh quantity of wood-spirit, acidified with youth of its bulk of sulphuric acid. In this way another portion of extract is obtained almost equal in quantity to the first. This last product has been employed and sold under the name of azala.

8. MM. Verdeil and Michel operate as follows:—The unground dried root is first steeped in water acidulated with sulphuric acid; next broken up by being squeezed and torn to shreds by means of fluted rollers. The material thus

obtained is submitted to hydraulic pressure, and steeped for forty-eight hours in a weak solution of carbonate of soda, sp. gr. 1'014=3° Tw. The material is again squeezed and thus freed from alkali, and the steeping is repeated with a weaker alkaline solution. The colouring matters, accompanied by some impurities, are precipitated from the alkaline solution by an acid. This precipitate having been collected on a filter, washed, pressed, and dried, is exhausted by boiling alcohol, and the filtered alcoholic solution precipitated with water. A similar mode of proceeding has been proposed by M. Schützenberger, with this difference, that he applies phosphate, or preferably, pyrophosphate, of soda instead of carbonate, thus obtaining a pure colouring matter. Good extracts of madder may be obtained by treating either garancin or flowers of madder with—(a) boiling acetic acid, sp. gr. 1.060, 12° Tw. The hot filtered liquid deposits, on cooling, abundance of a red flocculent matter; (b) by means of hot glycerin, which dissolves the colouring matters and deposits them on cooling; (c) by means of boiling benzin or rectified boiling sulphide of carbon, best applied under pressure with special provision against explosion and ignition; (d) by means of a boiling acidulated solution of alum, which dissolves the colouring matter, and throws it down on cooling. It is quite clear that none of these methods are commercially available in consequence of the expense and labour required.

We have now to mention some processes wherein water is used not to act upon the pre-formed colouring matter, but upon their soluble glucosides present in madder, which has not previously undergone any other operation than mechanical trituration, and is not too old. Mr. Higgin treats freshly ground madder with water containing from 3 to 6 per cent of its weight of acetate of lead and acetic acid, the lead salt being added with the view of preventing fermentation of the glucosides. The solution is filtered after standing for one hour; ammonia is added to the solution, which is thereby turned red; heat is applied, while a current of air is passed through to oxidise substances present, after which chloride of calcium is added for precipitation. The material thrown down is collected on a filter, washed, and decomposed by an acid, when the colouring matter is separated from the lime salt. A far more generally applicable method is that devised by M. E. Kopp, who applies sulphurous acid in aqueous solution; this solution, made in the usual manner, should contain from 4 to 5 or 51 thousandths of sulphurous acid. If the water is pure (relatively free from calcareous matter) there is added to this solution about from 1 to 1000 th of hydrochloric acid, in order to saturate the small quantity of carbonate of lime present even in the Alsace madder. If the water contain calcareous matter in larger quantity, more hydrochloric acid is required. The madder to be operated upon by this sulphurous acid solution should neither be pulverised too finely nor be simply coarsely broken up. In the first case filtration and expression are rendered more difficult, and in the latter the action of the liquid becomes unequal, and the operation of squeezing out is rendered almost impracticable. The madder is mixed with from ten to twelve times its weight of the sulphurous acid solution, placed in wooden tubs closed with tightly fitting covers, and left standing for from twelve to twentyfive hours, care being taken to stir the magma now and then. The semi-fluid mass is poured into a stout linen bag, and the tub rinsed out with a little clean water, which is added to the magma in the bag. The liquid is allowed to run off freely, and the bag gradually but strongly pressed; the clear fluid collected in a wooden tub; the contents of the bag are again placed in the tub from which they were first removed, and again treated with ten times their weight of sulphurous acid solution, and the yield added to the first obtained liquid. This operation is once more repeated, but the liquid is employed as an addition to the sulphurous acid solution required for a fresh portion of madder. The liquids run off should be carefully kept from contact of air, and poured into tubs closed with tight-fitting wooden lids. The madder, which has been exhausted with cold or tepid sulphurous acid, is placed in a vessel provided with a false bottom, pierced with small holes, over which is laid a stout piece of coarse flannel. The material is thoroughly washed out first with warm and then with boiling water. It now constitutes a weak fleur de garance, which yields on dyeing very pure tints, and leaves the whites thoroughly unsoiled. By adding from 3 to 5 per cent of sulphuric or hydrochloric acid to the sulphurous acid solution, and heating to 50° or 60°, a precipitate of raw purpurin is obtained, which is collected, washed with cold water to remove all the acid, and next dried. The remaining liquor, from which the purpurin has been removed, is boiled, when carbonic acid is disengaged, and a blackish-green pulverulent matter is thrown down, which is alizarin, stained with a very dark green substance, a product of decomposition of chlorogenin. The liquid should be kept at a boil for fully two hours in order to ensure the complete precipitation of all the raw or so-called green alizarin. The green alizarin is completely thrown down, and settles in from twentyfour to thirty-six hours. Since it is in a very fine powder it clings to the sides of the vessel, and only falls to the bottom on agitation. The supernatant liquid is run off, and the alizarin thrown upon a stout canvass filter, and thoroughly washed with cold water. When the boiling process has been carried on sufficiently long the dark yellow mother-liquor does not contain any more utilisable colouring matter. The alizarin is washed until all the acid is thoroughly removed. The crude material thus obtained is a most excellent dye stuff, readily manageable in the dye-beck, and yielding full bodied, very bright, yet deep colours, thoroughly fast and resisting cleansing and boiling soap lyes. The whites are scarcely soiled. Sometimes a small addition of chalk (0'I to 0'2) is advantageous in the dye-bath.

Several processes have been proposed to obtain pure alizarin from this, but none are readily practicable on the large scale, owing to the expense of the solvents, and from the difficulty of separating the impurities from large quantities of alizarin. The following process is the best and quickest:—

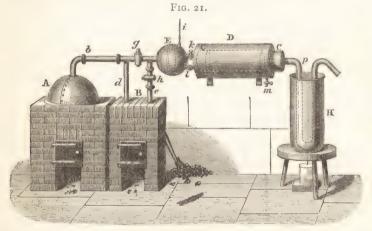
1 part of the raw alizarin is boiled with from 15 to 20 parts of light petroleum oil, boiling at about 150°. After about fifteen minutes' boiling the vessel is taken from the fire, and after standing for a few minutes, the clear liquid is decanted from the sediment. As soon as the decanted liquid cools it deposits a quantity of pure alizarin. When the temperature of the decanted fluid has fallen to 100°, there is added with careful stirring about 10 to 15 per cent of a solution of caustic soda, containing from 5 to 8 per cent of solid hydrate of soda. The soda takes up all the alizarin, yielding a purplish-coloured solution. The alkaline liquid is separated by decantation from the petroleum oil, and supersaturated with dilute sulphuric acid, which causes the precipitation of the alizarin in the shape of a crystalline magma, which is washed and dried.

The petroleum oil is next again applied to the same purpose; three or four treatments as described are sufficient to exhaust all the alizarin; the remaining greenish-black mass can be utilised for the preparation of a peculiar colouring matter (xanthazarin*), which possesses some curious properties. The pulverised greenish-black matter is gradually and cautiously introduced into a mixture of nitric acid with 10 parts of water heated to 100°, care being taken to avoid too strong action, and the quantity of the material being adjusted to three-fourths of the weight of the nitric acid employed. brownish-yellow matter hardly soluble in water is obtained. This xanthazarin is sparingly soluble in boiling water, very soluble in alcohol and ether, yielding a deep yellowish-brown coloured solution; with aqueous solutions of the caustic and carbonated alkalies it yields a very rich and brilliant orange solution. It dyes woollen and silken fibres very readily even without mordants, producing a deep golden-yellow colour. Cotton mordanted with alumina and dyed with this material assumes an orange-yellow colour. Reducing agents, viz., nascent hydrogen, sulphuretted hydrogen, hyposulphites. the protochlorides of tin and iron, deoxidise xanthazarin, and convert it into a red colouring material, which yields upon mordanted silken, woollen, and cotton fabrics colours approaching those produced by impure purpurin. Wool, previously dyed with xanthazarin a golden-yellow colour, assumes, when placed in a boiling solution of tin-salt, a carmine-red colour. The colouring material obtained by the reduction of xanthazarin is almost insoluble in water, and the shades it produces on textile fabrics are faster than those of the unreduced substance, which, however, stand ordinary washing.

M. Camille Keechlin was the first to suggest that alizarin might be directly obtained from madder by sublimation. The volatility of alizarin is, however, not very great, and its sublimation point is too near that of its decomposition by heat to make it practicable to sublime it from either madder, garancin, or fleur de garance, while if it were possible to overcome this difficulty an enormous quantity of empyreumatic matters would accompany the sublimed product, rendering its further purification troublesome and expensive. M. C. Keechlin and afterwards M. E. Kopp have endeavoured to obtain alizarin from madder or garancin by the aid of superheated steam. The apparatus employed by Kopp for this purpose, represented in the annexed woodcut, consists of-A, a steam boiler. b, steam pipe leading to B, a furnace for superheating the steam which enters by d; it leaves by e, a tube fitted with a stopcock, h. F, spherically shaped chamber, divided internally into two compartments by means of a perforated diaphragm, shown by a dotted line, and placed there to admit of a thorough admixture of the superheated with the ordinary steam, which latter is admitted by opening the stopcock g more or less. i, thermometer. cc, copper cylinder for containing dry garancin placed between two

^{*} Whilst madder root has been the object of a vast amount of research, the leaves, stem, seed, and that woody matter which intervenes between the root and the parts just named has been very little investigated. Many intelligent madder growers, both in Zealand and France, hold that the colouring principles are developed in the parts above ground, and returned to the root there to undergo further elaboration. Experiments have been undertaken to determine this question. Though these were never completed, it appears that the stems and seeds contain a substance closely related to xanthazarin. The first indications of alizarin in the plant are found about I inch below the soil. The woody part of the stem contains neither alizarin nor purpurin.

diaphragms; this cylinder receives steam (is in communication with the vessel **F** by means of the tube containing the stopcock k). D, another cylinder, serving as envelope for the last mentioned, and also in communication with r by means of a tube fitted with the stopcock l, which on being opened admits steam to D, the excess of which escapes by m. H, condensing apparatus, into which the products of the distillation are admitted by means of the tube b, which communicates with cc. When the furnace for superheating the steam has been heated to 360°, steam from the boiler at 180° (= 10 atmospheres, or 150 lbs. pressure to the square inch) is admitted into the cylinder D, and as soon as the cylinder c c and its contents have acquired that temperature the stopcock k is opened, by means of which superheated steam is admitted, first at a temperature of 200°, increasing gradually to 220°, 230°, and at last to 240°. The alizarin is volatilised, and carried by the steam in the shape of an orangeyellow coloured gas, which on condensing exhibits a powder of the same colour. When the operation is finished this powder is collected on a filter, while the condensed steam can be applied for dyeing purposes.



Madder lakes are insoluble combinations of the red colouring matters of madder with certain metallic oxides. Some of these are of great beauty, and employed by artists as oil and water colours, and they may be fixed upon textile fabrics, by the intervention of albumen, in the same manner as ultramarine, or they may be applied by being dissolved in a proper vehicle, say acetic acid, and thus used for calico-printing, because on expelling the solvent by steaming the pigment is fixed.

The only madder lakes which have obtained extensive application are those of alumina, the alizarate and purpurate. They are a more or less deep rose, with a slight—yet distinct and very characteristic—bluish hue. It is not easy to obtain really deep red coloured madder lakes in a dry state, owing to the great difficulty of obtaining alumina free from iron. These pigments yield fast colours, and are on that account esteemed in calico-printing. The principle of the preparation of these substances is that the madder pigments are dissolved by alum solutions, and precipitated by means of carbonate of soda. The following is M. Persoz's process:—Madder is washed with cold water

wherein some sulphate of soda is previously dissolved, and boiled for about twenty minutes with ten times its weight of a solution of alum containing 10 per cent of that salt as free as possible from iron. The liquid is filtered off from the insoluble dregs, and cooled down to 40° or 35°. The red-coloured solution can be treated either (1) by saturating cautiously with carbonate of soda equal to from one-eighth to one-tenth of the weight of alum used, so as to cause the formation of a basic alum to remain in solution. By bringing this fluid to a boil an insoluble subsulphate is thrown down, carrying along with it all the colouring matter contained in the solution: This precipitate is not gelatinous, separates readily, and is easily filtered; it is, moreover, entirely soluble in acetic acid. (2). By adding to the solution a suitable quantity of acetate of lead (78 parts of that salt for every 100 of alum employed), when sulphate of lead is precipitated. The red-coloured liquid, having been filtered, is boiled, when a basic sulphate of alumina is thrown down, combined with all the colouring matter in solution. The lake thus obtained is far deeper and more beautiful than that prepared with carbonate of soda. Instead of madder many of its commercial preparations can be applied for this purpose; among these may be noted purpurin.

It is quite clear that the preparation of madder lakes may be conducted by various other processes; for instance, the colouring matter could be dissolved in a limited quantity of alkali, and this solution saturated with hydrate of alumina. Hitherto the preparation of an iron lake from madder, suitable for printing purposes, has not succeeded. En passant, we mention here that alizarin ink is largely made in Germany; it is, of course, washed madder which is used for this purpose: it is intensely black, and very valuable, inasmuch as it is very fast and suitable for steel pens.

Testing of Madders, Fleur de Garance, Garancin, Extracts, &c.

We have already shown that a very large number of variable conditions exert, in some way or other, an influence upon the richness of any given kind of madder, in colouring material and the fastness of the colours produced. Sometimes madder is purposely adulterated with substances either added to increase the weight or with organic matters of no tinctorial value at all. Three points have to be kept in view for properly testing madder, viz.—(1), the value of the substance for the consumer under the conditions in which it is employed by him—a value depending upon the utilisable quantity of tinctorial matter present and upon the fastness and purity of the dyes produced upon the fabrics; (2), the absolute quantity of colouring matter present in the powder; (3), the testing for and quantitative determination of foreign and inert substances. Since the first point has the greatest interest to the consumer, it has been most studied, and we owe to M. H. Schlumberger a most practical—and at the same time most complete—process for its proper manipulation.

M. Schlumberger's process for estimating the utilisable tinctorial value of any kind of madder or garancin, and the test for the fastness of the colours produced, may be summarised as follows:—The principle of this mode of testing is a dyeing experiment, with a known quantity of madder and a known square surface of mordanted tissue, prepared—as used on the large scale—for red, rose-colour, and pink, with alumina mordants, and for black, lilac, and purple, with iron mordants. The result is compared with the effects produced

by a standard sample of madder of good quality. It is well to have an ample stock of that standard sample on hand, and to make simultaneously an experiment with it, while it is also advisable to weigh off at least two quantities of each sample to be tried, and experiment upon them at the same time. The relation between the mordanted surface of tissue and the tinctorial matter should be so regulated that the mordant be not quite saturated, so as to leave room for the evaluation of dye material, which perhaps might be better than the standard. On the other hand, the degree of saturation must be such as to admit of the proper estimation of the liveliness of the colours produced, and their fixity as regards the process of avivage or clearing: this latter operation is the more required to be performed with these samples, since it often brings the colours out in a manner different from their primitive brightness and intensity. The quantity of tissue—usually cotton—to be used in each experiment is 25 square centimetres, properly mordanted, and so treated as to be quite ready for use.* The quantity of madder is 10 grms., and of fleur de garance 5 grms., with a quantity of 1 litre of distilled water. When the experiment is to be made with Alsace madder, a little chalk has to be added to the water. The weighing off of the sample should be correct at least within I centigramme. The apparatus to be used and the manipulations to be employed are as follows: -The samples of cotton which are marked by slits at the margin, and the madder are placed in cylindrical glasses, capable of holding at least 1.2 litres, and made of well-annealed glass. These are placed together in a large copper, the top being closed by a copper lid, perforated with cylindrical openings large enough to admit the glasses to reach into the water. The best plan is to make the glass vessels rest on a perforated false bottom, and to immerse them to such a depth that only about \frac{1}{2} an inch projects out at the top. The glass vessels should not be placed in the water-bath until its temperature is 25°. At least two thermometers should be at hand: one to ascertain the temperature of the water-bath, the other to test now and then the temperature in the glass vessels. The heat is slowly raised from 25° to 95° during the lapse of two hours.† The latter degree is kept up for half an hour. It is very essential that a glass rod, not too thin, should be placed in each glass vessel, and the contents stirred every five minutes, care being taken to keep the cotton tissue entirely immersed and below the surface of the liquid. Every quarter of an hour the thermometer should be applied, to test the degree of heat inside each vessel: after the lapse of two and a half hours the pieces of tissue are removed from the baths, rinsed in cold water to remove adhering particles of madder or dye-stuff, then washed in cold water, squeezed out, dried, and ironed with a smoothing-iron as used by laundresses, and next cut with a pair of scissors in two equally sized parts, one of which is kept without further treatment, while the other is submitted to avivage or clearing. The first portion is pasted with one edge to a piece of paper, an open space being left for the other half to be pasted in afterwards. The first pattern of

^{*} On the Continent, in France and Belgium, tissue thus ready prepared and mordanted, in the shape of stripes running parallel with the width of the cloth, and ready for red, pink, violet, lilac, &c., is sold in several of the larger towns.

Where steam can be had it is best to apply that to heat the water, since it is more easily regulated than open fire: in the latter case charcoal and peat answer better than coals; gas of course, may be applied where it is to be had,

each sample is intended to exhibit the intensity of the tints produced before clearing, and also the degree of purity of the whites.

The process of avivage or clearing is carried on as follows:—(1), the samples are left for half an hour in a soap bath, made up—for eight samples of the size above stated—of 10 grms. of medium white soap and 4 litres of water, at a temperature of 75°; (2), boiling for half an hour in a soap bath of the composition just mentioned; (3), washing in cold water (that is to say, water of the same temperature as that of the place where the experiments take place); (4), the samples are next placed for ten minutes in a bath made up of 5 grms. of soap and 5 grms. of nitro-muriate of tin, in 4 litres of water at 45°. From this they are immediately transferred to a bath of boiling soap-water,—10 grms. of soap to 4 litres of water,—and kept boiling for half an hour. Next they are washed in cold water, dried, and ironed. By this process the solidity or fastness of the colours and their brilliancy may be judged.

M. G. Schæffer observes, as regards fleur de garance, that, since its use has become general, the tinctorial value of that material has in many cases been lowered. Fleur de garance is often met with which contains appreciable quantities of soluble organic matter and of sulphuric acid. It is quite evident that such products cannot possibly yield good results in dyeing, and among the tints which suffer most is the purple. The same authority states that the results obtained in testing fleur de garance do not represent so well as in case of madder the results obtainable on the large scale, especially when the sample is not well prepared, because the quantity of water used by the experiments on the small scale is about eight times larger than the quantity used on the large scale. Hence it is evident that the injurious effects of acid and of soluble matters present are less manifest in the experiments upon the small scale than in actual working. It is therefore required to test fleur de garance. previous to the dyeing experiment, for soluble matters. This is done as follows:-A quantity of some to to 15 grms. is thoroughly steeped in cold water, and the solid substance collected on a filter and washed. If the liquid which runs off is perceptibly coloured it is quite certain that the fleur de garance is not of the best quality. If chloride of barium produces this aqueous solution, which must be previously acidulated with a few drops of pure hydrochloric acid, a precipitate of sulphate of baryta will appear, indicating bad preparation. Such samples yield, when heated with sulphuric or hydrochloric acid, a very marked green colouration.

Fleur de garance, when properly prepared and carefully manufactured, gives hardly any colouration to cold water, and neither renders it acid nor capable of precipitating salts of baryta. If the sample is treated with sulphuric acid a rose colour is produced, and with hydrochloric acid a yellowish colouration.

It is best, when dyeing experiments are made with fleur de garance, to take of every sample two weighed quantities, and to add to one of these about one-fifth part of its weight of chalk, and leave the other sample to be operated upon without such addition. It is to be observed, also, that whereas with madder the temperature must be kept gradually rising, and neither falling nor remaining stationary, an irregularity of this kind is of no consequence with fleur de garance, while any irregularity with madder spoils the experiment. For 25 square centimetres of mordanted cotton tissue, as above specified, 1.6 grms. of garancin and $\frac{\pi}{4}$ litre of water are taken; in half an hour the

temperature is raised from 25° to 90°; afterwards the sample of cotton is first rinsed in cold and next washed in hot water, dried, and ironed. The same dyeing process as above described can be applied to test the value of extracts of madder, green alizarin, &c., with this understanding—that not only the quantity of such materials, but also of water, has to be modified. Resinous extracts should be first dissolved in a small quantity of alcohol, whereby the solution of colouring matter in the bath is promoted. As a general rule, the quantity of water to be employed in the process has to be decreased within certain limits, according to the higher degree of concentration of the tinctorial substance. For instance, with an extract from sixteen to twenty times stronger than madder, 250 cubic centimetres—{ litre—of water is sufficient for a surface of 25 square centimetres and the proper dose of dye material.

It is easily perceived that the process of test dyeing just described only yields results which can be compared with a standard sample, but the utility of this process is enlarged when dyeing experiments are made with decreasing quantities of the standard sample, the quantity—or rather size—of the cotton remaining the same. It is evident that—starting with 10 grms. of madder, 5 grms. of fleur de garance, and 1.6 grms. of garancin—a set of dyed samples may be produced, the colours of which, before as well as after the avivage, will be of less intensity, and we may thus construct a table or scale of colours, taking fleur de garance, for instance, as follows:—

No. I		 	* *	 	 5.00 8	grms.
No. 2	• •	 		 	 4.20	2.9
No. 3		 		 	 4.00	,,
No. 4		 		 	 3.20	11
No. 5		 		 	 3.00	2.3
No. 6		 		 	 2.20	2.2

and so on; and when an experimental dyeing result made with 5 grms. of fleur happens to be equal to between 2 and 3, we can say that 5 grms. of that fleur have a tinctorial value of from 4.5 to 4 grms. of the standard sample, or on average = 85, the standard being 100.

As regards the evaluation of the absolute quantity of colouring matter present in madder, none of the very large number of methods proposed for this purpose answer the object in view. These processes, moreover, are all of so complicated a nature, and require such a series of manipulations, that they are of no use whatever for practical work in dye establishments. M. Schlumberger has devised a method which gives satisfactory approximative results, and is based upon the dissolving power of acetic acid upon the colouring matter. Take 10 grms. of madder, which place in a suitably shaped glass vessel, e.g., a wide-mouth bottle; add 500 grms. of distilled water heated to 30°, and add a small quantity of beer yeast. Leave the mixture to ferment for twentyfour hours at a suitable temperature; filter off, and wash with distilled water, acidified with one-fiftieth of its bulk of acetic acid. Instead of the fermentation process, we may steep the madder in water acidified with acetic acid, for some hours, at 30°. Neither this operation nor that of fermentation is necessary when fleur de garance is to be tested. The residue left on the filter is boiled for ten minutes with a litre of very dilute acetic acid,-sp. gr. 1.005, or about 1° Tw.,-and decanted, after some rest pouring the liquid on a filter, and boiling the residue again with a fresh quantity of the same acid. These solutions deposit, on cooling, an orange-coloured flocculent matter, while some remains in solution, which is best precipitated by means of chloride of sodium. These sediments are carefully collected on a small dried and tared filter, washed with distilled water, carefully dried, and weighed.

By means of this process M. Schlumberger has obtained from 100 grms. of good madder (Avignon, Alsace, and Zealand) from 4.1 to 4.2 grms. of colouring matter. Inferior kinds-that is to say, second quality of the same origingave from 1.9 to 2.7 grms., while freshly-ground madder yielded from 3.8 to 4'2 grms. per cent, because, as regards the latter, the boiling with acetic acid has the effect of splitting up the glucosides, thereby making them equally rich in colouring matter as old madder.

The following mineral substances have been occasionally used to adulterate madder:-Ground-up red bricks, red and yellow ochres, yellow sand, and native coloured clays. Among organic substances the following have been sometimes used :- Sawdust of dark coloured woods, ground-up almond-shells, bran, fir-wood bark, logwood, santal wood, sapan wood, Brazil wood: as regards the mineral matters these may be readily enough detected, by the incineration of madder in a platinum crucible. It is best to take for that purpose from 5 to 10 grms., and to bear in mind that the quantity of ash (mineral matter) naturally present in madder varies from 5 to 9 per cent; in low class Mull madders it may reach 50. The qualitative testing of the ash will suffice to detect any fraudulent admixture.

As regards the adulteration with organic substances, we quote M. Pernod's plan for discovering their presence :- A piece of white paper is dipped for a minute or so in a weak aqueous solution of bichloride of tin; the sheet is placed on a plate glass, or on a clean porcelain dish, and by means of a fine gauze sieve a very small quantity of the pulverised madder is scattered on the surface. After the lapse of about half an hour every portion of the paper where a particle of the dye-wood has fallen will exhibit the following colourations :--

For Brazil wood Carmine-red specks.

.. Logwood Violet-coloured spots.

" Fustic Yetlow-coloured spots. " Genuine madder Faint yellow colouration.

If astringent substances have been added these may be readily detected by means of a sheet of test-paper impregnated with a mixture of proto- and persalts of iron, and moistened with alcohol. This paper, strewed over with the suspected madder in the manner as above, will, in case of adulteration, exhibit blackish-blue specks wherever any astringent matter has fallen. Pure madder yields in this instance only a bright brown colouration. The presence of foreign dye-woods in madder can also be ascertained by testing a hot filtered solution of madder with bichloride of tin or a per-salt of iron.

Use and Application made of Madder, and its Preparations for Dyeing Purposes.

The red colouring substances present in madder—that is to say, those which yield red colours with mordants of alumina-are its only really useful constituents. As regards the yellow and brownish matters, they only serve to

complicate the dyeing operations, and to diminish the beauty of the colours. These colouring substances do not admit of being directly fixed on textile fibres, the intervention of a mordant being an absolute necessity. Most of these mordants are metallic oxides, those chiefly used being the hydrated oxides of aluminium, peroxide of iron, and the sesquioxide of chromium. These oxides are incorporated with the fibre of the tissues by being brought into contact therewith as soluble salts, when they are precipitated and fixed in the fibre. The mordanted tissue, on being placed in a dye-beck containing the dye stuff, attracts the colouring matter, and combines with it in precisely the same manner as if the tissue were not present,—that is to say, that the affinities are only exercised between the colouring matter and the metallic oxide, while the tissue serves no other purpose than that of a framework in which both are mechanically held. There is thus formed a coloured lake adhering to the cloth, and the shade of colour, as well as its kind, varies with the nature of the oxide applied. This is red, rose, or pink coloured, when alumina is used; black, violet, or lilac, with iron, and chocolate, when a mixture of both these is made use of. Hence it follows that a dye-beck containing one and the self-same dye stuff (say madder) will produce, upon variously mordanted fabrics, very varying colours. In some cases a third substance is employed along with the madder pigments and the mordant, viz., a peculiarly modified fatty substance, as is the case in Turkey red dyeing, where this body gives greater stability and brilliancy of colour to the compound produced by the mordant and pigment. Generally the mordants are first applied to the tissue. This may, of course, be done in such a manner as to form designs and patterns by the aid of engraved rollers; after which the whole fabric is immersed in a dye-beck containing the madder, garancin, or fleur de garance, as the case may be, and treated as if it were to be uniformly

Madder colours are rarely printed directly on the fabrics. The use of madder and of fleur de garance implies some other operations after the textile fabrics leave the dye-beck, the aim of which operations is partly the bleaching or whitening up of those portions of the tissue which are intended to be left white, since it is not possible so to manage the dyeing process as not to soil, more or less, the portions of the fabric where no mordant at all is applied. On the other hand, the coloured portions have to be rendered bright and brilliant by soaping and clearing, whereby the colours are freed from such materials as would injure their beauty, viz., the yellowish substances present in the dye materials applied. When garancin, pincoffin, or any of the extracts of madder are used, the process of soaping and clearing (avivage) is not needed to the same extent, and a slight treatment with chlorine is quite sufficient to restore the purity of the white portions of the tissues. It should be observed that the colours are then less brilliant, less full-bodied and deep, than when madder is used and clearing employed. It depends, of course, upon the choice of the manufacturer, and upon the peculiar destination of the goods, whether madder, garancin, or fleur de garance is selected. When garancin or commercial alizarin is used, catechu can be applied simultaneously if desired, but this cannot be done with madder or fleur de garance, which require avivage.

The ordinary madder dyeing operation for the production of red (exclusive

of Turkey red), rose or pink, black, violet, and lilac of the highest brillancy, whether separately or conjointly, consists of the following separate manipulations:—(I). Bleaching the calico so as to render it perfectly white.

(2). Printing the mordants dissolved in a proper vehicle, and suitably thickened. (3). Fixation of the mordants—that is to say, the precipitation of the oxides—on and in the pores of the textile fibres. (4). Dyeing operation (garançage). (5). Avivage, or purification of the colours produced in the dyebeck: this may perhaps be designated as the process of modification of the colours by the introduction thereinto of a certain quantity of a fatty substance from the soap, and of oxide of tin from the salt of tin.

A. Bleaching.—We have previously entered into the details of this operation. What is especially required for this purpose is, that the operation shall be so perfectly performed that no foreign substance left in the tissue may, on the fabric being placed in the dye-beck, absorb so much of the colouring matter as to render the elimination thereof afterwards either impossible or impracticable.

B. Printing and Fixing the Mordants.—The operation of printing is a purely mechanical process, performed by highly complex machinery, the description of which is entirely beyond the scope of this volume. The substances used as mordants, and the methods whereby they are fixed, require our particular attention.

Mordants for Red-Pink, Rose-colour.

The substance used for this purpose is either a hydrate or a sub-salt of alumina. This material has to be intimately united with the fibre.

Alum is composed of sulphate of alumina and sulphate of potassa combined with water. There are two kinds of alum used in the arts. The greater part of the alum now met with in commerce, excepting what is yet made in the Papal States near Rome, is ammonia-alum. For the uses to which this salt is applied it is quite indifferent which of these two kinds is taken: the ammoniaalum is slightly more advantageous in strength. There are some cases where ammonia-alum cannot be applied, and where alum absolutely free from ammonia is required for use. By external appearance there is no possibility of distinguishing ammonia- from potash-alum; but if the sample is mixed up with caustic soda or slaked lime, ammonia-alum gives off the well-known pungent smell of ammonia. Alum in large crystalline lumps is more likely to be pure than that which is sold in powder, which often contains a small percentage of mother-liquor in excess, and more frequently traces of iron. Iron is the only impurity likely to cause trouble in alum: sometimes it is present in such quantities as to cause serious injury. As a test for iron, logwood liquor, tincture of galls, or a solution of ferro- and ferri-cyanide of potassium may be used. M. Persoz recommends, as a reliable test, the addition first of an excess of tartaric acid to the alum, and then caustic potassa in excess, when, a drop of sulphide of ammonium being added, the minutest trace of iron gives a black colour.

Potash alum (KO,SO₃+Al₂O₃,3SO₃+24HO) consists of potash, 9.95 per cent; alumina, 10.83; sulphuric acid, 33.71; water, 45.51. At 60° C. it loses 18 equivalents of water; fuses at 92° in its water of crystallisation, but is

only deprived of its entire quantity of water a little below red heat. Its solubility in water varies considerably, according to the temperature:—

100 parts of water at oo dissolve 3.39 parts of alum.

59	9.9	20°	93	12.13	2.2	7.9
9.9	23	40°	71	30.03	22	9.9
	**	100°	4.5	357.48	**	11

The solution of alum has a sweetish astringent taste, and exhibits an acid reaction. A concentrated aqueous solution of alum destroys the blue colour of ultramarine.

Ammonia-alum (NH₄O,SO₃+Al₂O₃,3SO₃+24HO) contains ammonia, 3.89 per cent; alumina, 11.90; sulphuric acid, 36.10; water, 48.11.

100 parts of water at oo dissolve 5.22 parts of this kind of alum.

9.9	11	20°	2.3	13.66	9.3	9.9	7.9
23	2.7	40°	2.2	27.27	91	99	23
	12	100°	22	421.00	22	22	9.9

When ammonia-alum is strongly heated, sulphate of ammonia, water, and sulphuric acid are driven off, while pure alumina is left behind: this property may, of course, be readily applied as a test.

Neutral or cubical alum (KO,SO₃+Al₂O₃,2SO₃) is obtained when 12 parts of alum and 1 part of slaked lime are boiled in water: on cooling, cubical-shaped crystals are deposited, which are valued in dyeing operations on account of their freedom from acid. The composition of such an alum is—Sulphuric acid, 33'95; alumina, 11'40; potash, 9'04; water, 45'61.

Sulphate of alumina—also known as cake alum, patent alum, and concentrated alum—is a salt manufactured on the large scale by dissolving previously calcined alumina (a pure clay, as much as possible free from iron) in concentrated sulphuric acid, the quantity of which is so regulated that there is rather excess of alumina. The formula of this salt is Al₂O_{3,3}SO₃+16HO. Notwithstanding yellow prussiate of potassa is purposely used for purifying this salt from iron, it is often found to contain some of that metal, and it is not unfrequently contaminated with Prussian blue. As regards its use in dyeing and calico-printing, it makes good red liquors, the technical name for those alumina mordants which yield red dyes with madder. It is stronger, weight for weight, than alum, containing at least a third more alumina, and consequently going further; but its composition is not constant, and the experience of all practical dyers and printers is that, although its use effects a saving of one-fourth of acetate of lead in the preparation of acetate of alumina, it is not by any means a suitable substitute for alum (potassa or ammonia), since it has been found that acetate of potassa and acetate of ammonia are of real use in the mordanting process: it is, moreover, by no means so easy an operation to get sulphate of alumina quite free from iron. According to Wildenstein, some of it contains even as much as II per cent of sulphate of protoxide of iron.

Nitrate of alumina and muriate or hydrochlorate of alumina (chloride of aluminium) are sparingly employed: they are made by mixing, in the first case, alum and nitrate of lead; and in the second, alum and chloride of calcium, known also as muriate of lime in the trade. Nitrate of alumina is easily decomposed, parting with its acid at a comparatively low temperature.

Some of the uses of nitrate of alumina depend more on its acting as a convenient acid salt than as an aluminous compound: thus it is used in blocking upon chrome oranges, to change them into yellow: its utility, in some steam colours, seems to be referable to the oxidising action of the nitric acid upon the colouring matter. On account of this ready splitting up of the elements of nitrate of alumina into acid and base, it must be sparingly and cautiously used as an ingredient in printers' colours. Chloride of aluminium, or muriate of alumina, resembles the nitrate with regard to stability, its solution acting nearly as powerfully as an acid, as if no alumina were present to neutralise the acid contained.

Acetate of alumina, or red liquor, made by mixing together acetate of lead and sulphate of alumina, or alum, is a very important mordant. When to a concentrated solution of sulphate of alumina a solution of acetate of lead is added, there is formed a precipitate of sulphate of lead, while the resulting liquid retains some of that salt in solution, which is got rid of by the aid of sulphuretted hydrogen and acetate of baryta. The solution of the acetate of alumina so obtained smells so strongly of acetic acid that it seems as if a portion only of the acetic acid had entered into chemical combination with the base. If spread out in thin layers, on plates of glass or porcelain, and heated to 37°, care being taken to keep the fluid constantly stirred, the salt dries up to a gum-like mass, easily re-soluble in water, but not exhibiting any longer the slightest smell of acetic acid. This product is considered by Mr. Walter Crum as a biacetate, while the liquor just alluded to is considered to be a mixture of acetic acid and this biacetate in aqueous solution. The solution of gelatinous alumina in boiling acetic acid, applied in excess, also yields the acetate here alluded to. The strongest solutions of saturated acetate, obtainable by double decomposition, contain about 5 per cent of alumina. When that solution, or also the solution obtained by dissolving alumina in boiling acetic acid, is left for several days standing at a temperature of 15° to 20°, it deposits on the sides of the vessel a solid substance, which after drying has the appearance of porcelain; and its composition is, according to Mr. Walter Crum, an insoluble biacetate containing five molecules of water. Another insoluble biacetate is obtainable in the shape of a crystalline precipitate. When a concentrated solution of red liquor, as first obtained by double decomposition, is heated, the supernatant liquid is almost entirely freed from alumina. The solutions of acetate of alumina obtained by double decomposition, and containing less than 3 per cent of alumina, are not precipitated by ebullition when they are freshly prepared, but after having been left standing for some weeks they acquire this property as soon as they contain as much free acetic acid as is equal to that contained in a saturated solution of acetate of alumina containing 4 per cent of alumina. When to red liquor such salts as, for instance, sulphates of soda, potassa, ammonia, magnesia, common salt, or alum, are added, they become far more readily turbid by the action of heat than when pure; but the solution of pure acetate of alumina is precipitated,—that is to say, becomes decomposed, and a basic salt thrown downwhen heated to 100°, while acetic acid is set free: the precipitate thus formed is re-dissolved on cooling, if care has been taken not to apply the heat so long as to expel the acetic acid which was set free.

Red liquor prepared with alum and acetate of lead, instead of sulphate of

alumina, consists of a mixture of acetate of alumina and an alkaline sulphate, and hence this preparation is more readily decomposed by heat than the pure acetate, which requires longer boiling and a certain degree of concentration.

For the preparation of neutral acetate of alumina, by means of alum and acetate of lead, 100 parts of the last-named salt require 62.6 of alum for complete decomposition, but very frequently in practice alum is applied in slight excess.

In Germany, a solution of alum is very frequently first converted into insoluble (basic) alum by means of carbonate of soda, and the resulting salt dissolved in acetic acid. Acetate of alumina is usually made by the comsumers, who often employ, instead of acetate of lead, the cheaper acetate of lime for the purpose of double decomposition, or also acetate of soda. Sometimes red liquor is purposely mixed with such salts as chloride of zinc, common salt, or chloride of ammonium, for the purpose of preventing the too rapid drying up of the acetate on the textile fibres. Acetate of alumina is also applied, on the large scale, to render woollen fabrics water-tight. If acetate of lead be mixed with alum and hot water, and cotton cloth then passed in it, it takes up alumina in sufficient quantity to dye with. In mordanting woollen cloth, cream of tartar (bitartrate of potassa) is used to mix with the alum, and here a similar decomposition takes place; the sulphuric acid goes to the potassa, leaving the tartaric acid to the alumina, from which the wool can take it up easily. The acetate of alumina does not answer so well for woollen fabrics as the tartrate, perhaps because it gives up its alumina too readily, whereby the mordanting is rendered superficial and uneven.

Aluminate of potassa is known as alkaline pink mordant, Alumina, in the hydrated gelatinous state, is readily soluble in caustic alkalies. If caustic potassa is added to a clear aqueous solution of alum, with the precaution not to overdose the alkali, there is at first precipitated gelatinous hydrate of alumina, which re-dissolves on adding more alkali. On the large scale this solution is made by taking a sufficient quantity of a solution of caustic potassa, sp. gr. 1'307 to 1'41 = 40° to 50° Tw., and heating nearly to boiling in an iron pan. The requisite quantity of alum or sulphate of alumina, in coarse powder, is put in by degrees, the heat of the liquid being kept up, and the whole well stirred. Finally, it should be boiled a short time, say fifteen minutes, and then allowed to cool. Crystals of sulphate of potassa are deposited, which are very sparingly soluble in the alkaline liquid. Another sediment, of a light colour, is found at the bottom of the pan, consisting of alumina not dissolved. About 31 lbs. of alum to a gallon of caustic lye, at 40° Tw., is a proper proportion: if sulphate of alumina be used the same quantity may be taken, but the caustic liquid should be more concentrated, ranging from 50° to 55° Tw. Practical experience has taught that ammonia-alum will not answer for this purpose, since more caustic lye is required to drive off the ammonia. Alumina hydrate may be made first, and then dissolved in caustic lye. This is a more scientific as well as a more economical method, since no alkali would then be required for combining with the sulphuric acid of either alum or sulphate of alumina.

Aluminate of potassa should be kept in a covered vessel, since it is injured by lengthened exposure to air: it is preferably kept in vessels made of iron, since it attacks glass, earthenware-jars, and wood. The addition of acids or acid

salts to this solution causes precipitation of the alumina. The carbonic acid of the air also slowly causes the decomposition of this liquor, especially if it is exposed in thin layers: most of the neutral salts, when mixed with this fluid, precipitate the alumina, as, for instance, sal-ammoniac, the sulphates of magnesia and zinc, and all other soluble metallic salts. This reaction is made use of in the process of mordanting with aluminate of potassa, since the cloth previously impregnated with this liquid is dunged, with the addition of some of these salts to fix the alumina, sal-ammoniac or a salt of zinc being preferred. The oxide of zinc simultaneously precipitated has very little affinity for the cloth, and is detached in washing, but any iron salt present is decomposed and deposited in the fibres along with the alumina, and, according to the quantity present, it dyes up with madder a dull chocolate instead of red.

Aluminate of soda is largely made and used in France, since the discovery of the extensive deposits of bauxite in the southern parts of that country. It is obtained by roasting, in a reverberatory furnace, a mixture of soda-ash and bauxite, until a small sample taken from the fritted mass ceases to effervesce with acids. When the operation is finished, the aluminate of soda is extracted by lixiviation with boiling water, and the solution evaporated to dryness. It is a coarse powder, exhibiting a slightly greenish colour, due to a trace of vanadium. It is infusible at the highest furnace-heat, and readily soluble in hot and cold water. Dilute solutions (sp. gr. 1.072 to 1.089 = 14 and 17° Tw.) remain limpid and clear for a long time, but stronger solutions (sp. gr. 1.3 to 1.37 = 62° to 71½° Tw.) deposit granular alumina, while the supernatant liquor contains a subaluminate and excess of caustic soda. This aluminate of soda agrees in its properties with the corresponding potassa salt.

Since bauxite is a very pure native hydrate of alumina, the aluminate of soda prepared with it is used for the production of acetate of alumina in the following manner:—The aluminate of soda is precipitated by the addition of a very slight excess of hydrochloric acid; the gelatinous alumina thus obtained is thoroughly washed with boiling water, and next dissolved in acetic acid. The percentage composition of the pure aluminate of soda is 47'21 soda and 52'79 alumina; the commercial product, as met with in the French market, is contaminated with about 9 per cent of impurities, due to the presence of sulphate of soda and chloride of sodium in the soda-ash.

As regards the methods of fixing alumina upon woven fabrics, it must be in a perfect state of solution, while it is also necessary that the hydrate of alumina should be precipitated, in the best possible physical condition, within the fibre of the fabrics. W. Crum found that the microscopic examination of fibres mordanted with acetate of alumina and dyed, and similar fibres mordanted with chloride of aluminium and dyed, presented differences, inasmuch as in the first instance the coloured lake, or combination of alumina and colouring matter, was chiefly accumulated within the central canal of the fibre; in the second case, however, the periphery of the fibre only was coloured.

Alumina can be obtained in solution—(1), in the state of a saline solution of that base; (2), as a basic salt; (3), as a soluble modification of the earth itself; (4), in combination with alkali. Some of the salts of alumina can be brought into contact with the cotton fibre without any decomposition

whatsoever ensuing, so that a simple washing in cold water eliminates all the alumina taken up. This happens, e.g., with nitrate and sulphate of alumina and with alum. Whenever it may be desirable to apply such salts for the purpose of mordanting cloth it is necessary to pass the cloth, after it has been impregnated with the aluminous solution, through a bath containing substances capable of precipitating within the fibres either hydrate of alumina or at least an insoluble basic salt of that base. Some of the salts of alumina are decomposed by moist heat (steam), thereby giving up to the fibres of the cloth the whole or a portion of the alumina, or becoming converted into a basic salt. The acid set free is volatilised, or leaves the tissue. chloride, acetate, and hyposulphite of alumina are salts of this description. These salts become fixed by exposing the saturated tissues to a warm and moist atmosphere. This result is not simply a dissociation of the constituent elements of the salt, but the intervention of the water is absolutely required for the formation of the hydrate of alumina. The action is therefore to be considered as a saponification, in the more extended sense of this word as understood by chemists.

It is here the proper place to give a few particulars concerning the process just mentioned, and known as "ageing." The mordants generally used for madder styles are the pyrolignites, or acetates of iron and alumina, which under the influence of ageing-which we are about to describe-are so decomposed as to leave on the cloth either an insoluble oxide or a sub-salt, which becomes the intermediate agent for fixing on the fabric the colouring matters of madder. The fixing of mordants by ageing was first practically carried out by Mr. Walter Crum, an eminent and highly scientific calicoprinter. On the proper ageing of printed goods, says Dr. Schunck, depends in a great measure the success of many styles. Should a room be too hot or too dry, imperfect fixation of the colour ensues, and meagre and uneven tints are obtained in the subsequent operations. To give some idea of the importance of this step in calico-printing, we may here state that "ageing rooms," as they are called, are in several print-works of enormous dimensions, and generally constitute a separate building. Those of Messrs. Edmund Potter and Co. and Messrs. T. Hoyle and Sons, all at or near Manchester, may be particularised as forming quite a feature in their works. The process of ageing in calico-printing is that by which a mordant, after being applied to a cotton fabric, is placed in circumstances favourable to its being completely incorporated with and fixed in the fibre. It has generally been found desirable that calico printed with a mordant should, before dyeing, be exposed to the atmosphere for some time in the ageing room, in single folds, which, generally speaking, requires several days, the object being to liberate the acetic acid from the acetates of iron or subacetates of alumina, and to oxidise the protoxide of iron. It was for many years believed that oxygen was the only necessary agent; and although some printers had observed that moisture facilitated the process, this fact was not generally known until Mr. J. Thom, of Manchester, claimed the introduction of moisture as an important agent in the process of ageing, in a patent which he took out in 1849. Mr. Walter Crum was, however, the first printer who applied this principle practically. He describes the process as adopted at Thornliebank (near Glasgow) in the following words: A building is employed 48 feet long

inside and 40 feet high, with a mid-wall from bottom to top running lengthwise, so as to form two apartments, each II feet wide: in one of these apartments the goods first receive the moisture they require. Besides the ground floor it has two open sparred floors, 26 feet apart, upon each of which is fixed a row of tin rollers, all long enough to contain two pieces of cloth in their breadth. The rollers, being threaded, are set in motion by a small steamengine; and the goods to be aged, which are at first placed in the ground floor, are drawn into the chamber above, where they are made to pass over and under each roller, issuing at last at the opposite end, where they are folded into bundles on one of the three stages which are placed there. These stages are partially separated from the rest of the chamber by woollen cloths. While the goods are traversing these rollers they are exposed to heat and moisture, furnished to them by steam, which is made to issue gently from three rows of trumpet-mouth-shaped openings. The temperature is raised from 80° to 100° F., or more, a wet bulb thermometer indicating at the same time 76° to 96° F., or always 4° less than the dry bulb thermometer. In this arrangement 50 pieces of 25 yards each are exposed at one time, and, as each piece is a quarter of an hour under the influence of steam, 200 pieces pass through in an hour. Although workpeople need scarcely ever enter the warmest part of this chamber, a ventilator in the roof is opened when there is any considerable evolution of acetic acid. The mordant does not, however, become fully "aged" by this process alone, although it is acted upon as much as if it had hung a whole day in cold air. It has received, however, the requisite quantity of moisture, about 7 per cent of the weight of the piece, and is thus enabled, if the mordant be iron, to take oxygen from the air, and to become changed with time into the sesquiacetate and sesquihydrate of oxide of iron. In order to be sufficiently aged it must be left one or two, or even three, days in an atmosphere still warm and moist.

It had been ascertained long before, at Thornliebank, that exposure in single folds after moistening was not necessary. The experiments of the late Prof. T. Graham, on the diffusion of gases through small apertures, had served to suggest that, for the absorption of the small quantity of oxygen required, the goods might as well be wrapped up and laid in heaps. Accordingly, in the operation in question, the moistened goods are carried in bundles into the building, on the opposite side of the mid-wall already mentioned, and laid upon the sparred floors, placed at heights corresponding with the stages in the first apartment. Upon these floors 7000 or 8000 pieces may be laid at a time, and, since each piece is 25 yards long, 100 miles can be stored at once. It is necessary, of course, that an elevated temperature and a corresponding degree of moisture be preserved in the storing apartments, day and night, and 80° F. is sufficient, with the wet bulb thermometer at 76°. To effect this condition a large iron pipe is placed along the ground floor underneath, and moderately heated by steam, while a row of small jets in the same position are made to project steam directly into the air of the room. The whole building is protected from external cold, and consequently from condensation of steam, by a warmed entrance room, and by double windows, thick walls, and a double roof. Small steam-pipes are also placed at other points where they seem to be required, and the apartment which contains the rollers is specially heated, when not in use, by a couple of steam-pipes, which are placed under the ceiling of the ground floor.

The process of ageing, as thus detailed, was in operation at Thornliebank in the autumn of 1856. About a year afterwards it began to be adopted by other printers, and now it is pretty generally used in the best arranged printing establishments in Scotland and in Lancashire. The basic salts of alumina readily yield to the textile fabric the excess of alumina they contain, and become thereby converted into neutral saturated salts. Heat and moisture, in this case, aid the attraction exerted by the porosity of the fibre. As regards alkaline aluminates they are applied as mordants,—that is to say, the alumina they contain is fixed to the fibre by (1), simple exposure to the open air, when the carbonic acid of the atmosphere saturating the alkali causes the deposition of alumina; (2), the cloth is passed through a very dilute acid solution, too weak to re-dissolve the alumina, sour buttermilk being sometimes used for that purpose in Switzerland and Holland; (3), by causing the cloth to be passed through an aqueous solution of ammoniacal salt; alumina does not combine with ammonia, which is of course hereby volatilised; (4), by immersion in a solution of a metallic salt, the oxide of which forms an insoluble aluminate with alumina.

The preparation of the red liquors as used for madder work has undergone a great number of variations and improvements since calico-printing and dyeing were first introduced into Europe. Many manufacturers use alum and white or brown acetate of lead as the chief ingredients; others, again, apply sulphate of alumina, free from iron, like that obtained from bauxite. The alkaline aluminate is not very frequently used. There is much difference of opinion as regards the preparation of the red liquor. According to pure theoretical views the quantity of acetate of lead should be so regulated that all the sulphuric acid of the neutral sulphate of alumina contained in alum is precipitated as sulphate of lead, leaving in the liquor acetate of alumina fully saturated, and, if alum has been used, sulphate of ammonia or of potassa. There is no reason for using excess of acetate of lead so as to convert also the alkaline sulphates into acetates. Since this opinion was defended by M. Sébille, who advised the use of 125 parts of acetate to 100 of alum, M. D. Keechlin-Schouch has put this matter to practical test, by using the same quantity by weight of alum and of water, with variable quantities of acetate of lead, when the proportions of this latter salt varied as much as from 75 to 125 parts for 100 of alum, the quantity of water remaining the same. dyes obtained did not exhibit any difference at all. Below 75 the shades became weaker, when the quantities of acetate of lead and water were left the same and the quantity of alum varied: it was found that the strongest mordant was formed when 3 parts of acetate to 4 of alum were used. The theory of M. Sébille would require 5 parts of acetate to 3 of alum. It is clear that these observations extend to sulphate of alumina as well, care being taken to alter the ratios; and we may therefore safely conclude that there is no need whatever to carry the double decomposition on to the point of complete exchange, and that a certain quantity of sulphuric acid may be left in the liquid without fear of affecting injuriously the strength of the mordant. What is contained in the mordant prepared with 100 parts of alum and 75 of acetate of lead cannot at present be determined with perfect certainty. In other words, we do not know anything certain about it. All that can be said is, that the two acids present partake of the base in proportion to their bulk. Take the case of a mordant simply prepared with sulphate of alumina: this

will contain, after removal of the sulphate of lead by filtration, a variable quantity of basic sulphate of alumina, according to the greater or less amount of sulphuric acid which has escaped precipitation, and also basic acetate of alumina and free acetic acid, which keeps both these basic salts in solution. When this liquid is printed on cloth it begins speedily to give off volatile acetic acid, and the basic salts are fixed on the tissue, the process being completed by ageing.

According to the direct experiments made by M. D. Keechlin, the basic sulphate of alumina has been proved to be an excellent mordant. He prepared this salt by partial precipitation of a hot and concentrated aqueous solution of alum, by means of caustic potassa. The salt obtained was dissolved in a sufficient quantity of acetic acid, and the liquid was used for printing, and the tissue exposed to ageing. It is quite clear that nothing but subsulphate (basic sulphate) of alumina could remain on the cloth after drying, since the elimination of the acetic acid must have been complete, and the sulphuric acid could not, under any conditions, leave the base or the cloth. This cloth, after having been dunged, was put in the dye-beck, and gave excellent results. This experiment proves that we may admit, at least, that as regards the ordinary mordants there remains on the cloth, after printing and ageing, a certain quantity of subsulphate of alumina, which contains all the sulphuric acid of the neutral sulphate of alumina which has not been combined to sulphate of lead plus a certain dose of alumina or subacetate of alumina derived from the acetate of that base decomposed during the ageing process. When exactly 100 parts of alum and 75 of acetate of lead are employed, about two-thirds of the sulphuric acid of the sulphate of alumina are displaced: the composition of the liquid which is the result of this reaction is represented by a liquid prepared by dissolving I molecule of basic sulphate of alumina in 2 molecules of acetic acid. Whether or no the two acids do temporarily each partake of a portion of the base present, after the ageing process there will only be basic sulphate of alumina left on the cloth. These considerations, which somewhat elucidate the true nature of the mordants, do not clash at all with the use of pure acetate of alumina. What is said is only meant to prove that the subsulphate of alumina, and the sulphates of soda, potassa, and ammonia, or also the alkaline acetates, can be mixed along with the acetate of alumina without injuring its excellent properties as a mordant. We may also state here that, as regards the materials to be used, the purest articles answer the purpose best in every respect.

The following prescriptions for red liquors are given by M. D. Keechlin:-

Strong Mordant, No. 1.

30 gals. of water, 6 of which are a decoction of Lima-wood to "sighten" the work; 165 lbs. of alum; 16½ of soda-crystals; and 165 lbs. sugar of lead.

Mordant, No. 2.

Water as above; 82½ lbs. of alum; 8½ lbs. of soda-crystals; 55 lbs. acetate of lead.

These formulæ are old. The following are of more recent date:-

Strong Mordant.

11 kilos. alum; 82.5 grms. acetate of lead; 32 litres boiling water.

5/4 Mordant.

625 grms. alum; 450 grms. acetate of lead; 2 litres boiling water.

The following mixtures are in great repute with some dyers:—

Alum			A. 16 kilos.	B. 8.o kilos.	C. 10 kilos.
Acetate of lead				8.5 ,,	10 ,,
Boiling water			62 ,,	60.0 ,,	20 ,,
Extract of Lima-v	vood	, at			
20° Baumé			2 ,,	4.0 ,, (at 3	°)
			30° Tw.	4° Tw.	

In England it is customary to make up the mordants without the peachwood liquor, and only add it when the colour is being prepared for printing.

> Red Mordant (Liquor) for Garancin, At 11° B.=1'083 sp. gr.=15° Tw.

25 kilos. alum; 19 kilos. of acetate of lead; 80 litres of water.

Strong Mordant, At 11° B.

2.5 kilos. alum; 2 kilos. acetate of lead; 6.3 litres of water.

Mordant for Red with Garancin.

Alum, 16:08 kilos.; acetate of lead, 12:08; water, 40:16 litres.

According to the experiments of M. D. Kæchlin, the mordant No. 2 (just mentioned) is strong enough to furnish, with nearly all tinctorial substances, the strongest tints which they can produce consistent with complete saturation. Instead of keeping one standard mordant, which, by being diluted with water, might serve to produce the different shades desired, the manufacturers prefer to prepare a series of mordants graduated in strength according to the style of work intended. The reason for this system is, that a strong mordant does not keep so well for any length of time; moreover, since all these kinds of mordants, even when kept in well-stoppered vessels, deposit in time more or less acetate of alumina, which is not readily again taken up in acetic acid, it is convenient not to prepare too much of any of these mordants at once.

Pure acetate of alumina in solution can be heated to the boiling-point without decomposition, or without throwing down any basic salt, but the mordants containing sulphate of potassa or basic alum become turbid on heating, and yield an abundant precipitate, which re-dissolves on cooling. According to Gay-Lussac this precipitate is hydrate of alumina; but since M. D. Kæchlin found it to consist of 100 parts of sulphuric acid and 343.5 of alumina, it should be considered as a mixture of alumina and a basic sulphate of alumina. It is an interesting fact that the formation of this precipitate takes place at a lower temperature, and more abundantly in the weaker mordants than in the stronger. The solution of subsulphate of alumina in acetic acid, obtained by partially precipitating at boiling heat a concentrated solution of alum with caustic potassa or soda, yields a good mordant.

If it is needful to prepare a solution of acetate of alumina with sulphate of alumina, the process is first to make a solution of the sulphate at from 31° to

33° Baumé = sp. gr. 1.275 to 1.298 = about 50° to 55° Tw. From 110 to 115 parts of this solution are precipitated by 100 parts of acetate of lead previously dissolved in 30 parts of water: the resulting liquor has, after filtration, a strength of from 1.116 to 1.125 sp. gr. = about 21° to 23½° Tw., and contains from 18 to 19 per cent of acetate of alumina. This is the highest strength attainable; and the liquor yields, when employed as a mordant, the same result as that obtained from alum, provided the sulphate be quite free from iron. It has already been observed that, instead of acetate of lead, acetate of lime is frequently used in this process: 100 parts of alum, 100 of water, and 150 of crude acetate of lime solution, sp. gr. 1.087 = about 15½° Tw., yield a red liquor having a strength of sp. gr. 1.095 = about 18° Tw. Excess of lime must be avoided, since it renders the colours dull.

M. E. Kopp has called attention to the use of hyposulphite of alumina as a mordant. This salt is perfectly soluble in water, and the solution is decomposed at a boiling heat into sulphurous acid, sulphur, and alumina. None of these compounds can affect the strength or quality of the fibre to which it is applied. Pure hyposulphite of alumina may be prepared by the double decomposition of crystallised sulphate of alumina and crystallised hyposulphite of lime. Of the first-named salt take 4.167 kilos., and after solution in water there is added a solution of 4.875 kilos. of the latter salt. The precipitate of sulphate of lime is removed by filtration through stout flannel, and the precipitate strongly pressed: there is thus obtained a perfectly clear solution, which can be preserved for a long time, even in contact with air. A solution of hyposulphite of alumina of 1.20 sp. gr. contains as much alumina as a solution of acetate of 1'10 sp. gr. The solution of hyposulphite is readily thickened in the cold by means of gum, torrified starch, or British gum. The hyposulphite solution resembles the acetate solution in this respect, also, that it is better for being not quite pure and more advantageously used when mixed with a certain proportion of alkaline salts: 6 kilos. of alum are completely decomposed by the use of 4.65 kilos. of hyposulphite of soda, or 4.85 kilos. of crystallised hyposulphite of lime, so that 2 kilos. of this last salt can replace 3 kilos. of acetate of lead, which latter is obviously a far more expensive salt.

Since there is some difficulty in thickening sulphates with starch, M. Kopp advises to prepare first hydrochlorate of alumina, which, in the state of a thickish syrup, is incorporated with cold starch paste. To this mixture is next added hyposulphite of soda, in such proportion as to decompose two-thirds or three-fourths of the hydrochlorate of alumina. In order to prepare a hydrochlorate of alumina suitable for this purpose, it is proper to decompose 6 kilos. of ammonia-alum in aqueous solution, by means of 2.78 kilos. of dry chloride of calcium (not chloride of lime). The liquid, after being drawn off from the precipitated sulphate of lime, is evaporated to the consistency of a syrup in a leaden vessel. On cooling, there are formed crystals of sal-ammoniac; the mother-liquor is drawn off, and evaporated at 150° until a pellicle forms on the top of the liquid, which, on cooling, becomes a solid, white, deliquescent mass. M. Kopp prepares hyposulphite of lime by the action of sulphurous acid gas upon a previously boiled mixture of basic oxysulphide of lime (soda waste), with 10 per cent of its weight of pulverised sulphur and water. As soon as the liquid shows an acid reaction it is neutralised and allowed to stand till clear, and evaporated at a gentle heat. In this way beautiful

crystals are obtained. When this salt is precipitated, in aqueous solution, by sulphate of soda, hyposulphite of soda is formed, which crystallises readily. The hyposulphite has the following advantage as a mordant over the acetate of alumina: -(1), it is more economical, especially when mordants are required which are either not thickened at all or but slightly; it yields, when equal in strength to the acetate, more full-bodied colours; (2), it is more rapidly and completely fixed than any other alumina mordant; (3), it prevents, to a certain extent, the fixation of iron, because, as long as there remains hyposulphite of alumina undecomposed in the fibres, any iron which may be contained in the preparation (mordant) is kept in the state of protoxide, and cannot adhere permanently to the fibre. Only after the complete decomposition of the hyposulphite can oxidation of any iron compound present set in, and its fixation take place. Notwithstanding these advantages, against which has to be set the slight inconvenience of the evolution of sulphurous acid in the ageing rooms, the hyposulphite is hardly, if ever, now used. The general opinion of English printers is, that the hyposulphite does not present any marked advantage over the common red liquors.

We now come to another point, viz., the methods of thickening these mordants without injuring their properties. We have already stated that one and the same mordant, thickened to the same degree with different thickeners, does not, on dyeing, yield results of the same value. Gum Senegal especially and also some of the gums known as Arabic gums do not act well for the fixation of an aluminous sub-salt. Moreover, two mordants of the same strength, but thickened with different substances, give shades which vary in beauty and intensity. It is, for instance, well known that a mordant thickened with starch paste combines more readily with the cloth, and yields deeper shades than the same mordant thickened with gum; but for certain kinds of colour gum is preferable, since it gives more transparency to the colours, while a portion, however small, of the starch-paste remains always with the mordant, notwithstanding the clearing process. The difference in the intensity of a colour may arise from the increase of bulk caused by some thickeners which have to be used in larger quantity, in order to obtain an equal consistence, and this causes, as it were, a greater or less distance between the particles of alumina. Any mordant strongly thickened with gum dries too rapidly, and combines only slightly with the fibre, thereby causing a weakness of the colours. The consistence of a mordant can be readily increased, by means of starch or farina, without any such undesirable results ensuing. A strong and simultaneously acid mordant is not readily thickened by means of starch, and the liquid does not then acquire a sufficient consistency, and it is therefore far better to thicken it with gum or torrified starch. A mordant which contains an excess of alum (2 parts of alum for one part of acetate of lead), if thickened with starch, attracts water even after the lapse of a single day. Hence it may be readily seen that the degree of consistence and the nature of the thickening substance must vary, and are accordingly regulated by the kind of printing to be done, the specific gravity, and the quantity of the acetate contained in the mordant. The thickeners usually applied for red and pink colours are white starch and roasted starch. When starch is used it is necessary to boil the liquid, which causes the precipitation of a sub-salt of alumina, which, however, remains suspended by the viscosity of the liquid,

and becomes re-dissolved on cooling, especially if well stirred until quite cold. It should not be used hot. When it is required to dilute the mordant with much water, as for instance for light rose-colours, it is best to thicken the water first by means of starch, and to add next the mordant to that mixture when nearly cold. The following are prescriptions of thickened mordants for red and rose-colours, ready made up for printing with the cylinder-machine.*

Deep Red. Medium Red. Bright Red.

	-		-
Acetate of alumina at 9° Bau = 1.067 sp. gr. = 13° Tw.	> 1 HHG	I litre	1 litre
Water	I ,,	4 litres	15 litres
Starch	240 grms.	0	О
Roasted starch	60 ,,	2 kilos.	6 kilos.
Gallipoli oil (huile tournante)	30 ,,		
Decoction of Lima-wood	164		

Red Mordant for Madder.

Garancin morda	ant at	IIº	Baun	né				 	I litre
White starch								 	110 grms.
White-coloured	roast	ed s	tarch	(B	ritish	gum)	 	75 33

Bright Red.

Strong mordant at 11° Baumé (see above)	I litre
Acetic acid† at 2° B. = 1.007 sp. gr. = 1½° Tw	4 litres
Solution of British gum containing 750 grms. to the litre	9 ,,
Pipe-clay water containing 1 kilo. of pipe-clay to the litre	5 ,,

Red Mordant for Deep Red.

(For fine designs).

		_								
Acetate of alun	nina at 9°	В.							1.0	litre
Water										
Brazil-wood de	coction								10.0	22
Acetic acid (as										
Alum										
Pyrolignite of I	ead (crude	e ace	etate)						2.2	10
White starch									3.0	83
Gallipoli oil (hi										
Solution of niti	rate of cop	pper	at 52	° B.	=1.	547 9	sp. gi	:)	375	
= 1091° Tw.)	3/3	77

Note that the sulphate of lead which is formed remains in the mixture, serving the purpose of giving body, and thereby aiding the regularity of the execution of the fine designs.

^{*} See D. Kœchlin-Schouch, Sur le Mordant Rouge, "Bulletin de la Société Industrielle de Mulhouse," vol. i., p. 277.

[†] It should be borne in mind that the specific gravity of vinegar and of acetic acid is no proper test for their goodness; acetic acid is specifically lighter than water; vinegar, according to its origin, contains a variety of other substances in solution along with acetic acid and water. The quantity of acetic present in vinegar varies from 2 to 8 per cent.

Ad

Red Liquor, or Mordant.

	Red Liquor	, or I	viora	ant.				
	White starch						2 kilos	3.
	British gum						4 ,,	
	Strong mordant (see p. 284)	,					10 litre	S
	Lima-wood extract at 31° Tw.						1 litre	
	Gallipoli oil (huile tournante)						1 2 22	
	Pyroligneous acid (crude acetic)					5 litre	S
	Hydrochloric acid					0.0	1 litre	
	Pyrolignite of lime						τ kilo	
ld v	hen cold—							
	Tin-salt						750 grms	3.
	Other Red M	Iordaı	at (R	led .	4).			
	Mordant A (see p. 284)						20 litre	S
	White starch						6 kilos	3.
	Gallipoli oil						250 grm	s.
	Turpentine (oil of)						250 ,,	
	Re	d 4/2	•					
	Mordant A (see p. 284)						24 litre	es.
	Water						6 ,,	
	White starch						6 ,,	
	Gallipoli oil						250 grm	s.
	Turpentine (oil of)	* *					250 ,,	
	Mordants for R	ose-C	Color	ır (F	Pink) -		
	Boiling water		301	litre	S		38 litre	S
	Acetic acid at IIIº Tw		I	29			2 ,,	
	Mordant 5/4 (see p. 284): 625	grnıs.)					
	alum, 450 grms. acetate of		- 8	9.9			21/3 ,,	
	2 litres boiling water							
	Dark roasted starch		20				20 kilo	
	Gallipoli oil						375 grm	ıs.
	Turpentine (oil of)		375	22			375 "	

In all these cases the acetic or pyroligneous acid must be well mixed with the mordant before adding it to the water, starch, &c. This is especially important for light shades.

It is quite clear that these prescriptions are varied in different ways, and differ not only in different countries, but also according to the experience and taste of the manufacturers: those above quoted are all French. The following are English, but are stated to have been prepared in accordance with principles laid down in M. D. Kæchlin's paper on red liquor already alluded to:—

	No. I.	No. 2.	No. 3.	No. 4.	No. 5.	No. 6.
Water, gallons	45	45	45	45	45	45
Alum, Ibs	100	100	200	190	190	129
Acetate of lead, lbs.	100	129	200	190	129	100
Crystals of soda	10	IO	IO	19	0	0

The alum, previously ground, is dissolved in the water heated to 140° F.; the crystals of soda are next dissolved with stirring, and then the acetate of lead added in coarse powder, and the whole well stirred for a considerable time, and afterwards at intervals during two or three days. Nos. 1 and 2 are common reds for calico, No. 2 being better adapted for a gum colour and for blocking than No. 1; Nos. 3 and 4 strong mordants, suitable for muslin or light goods; Nos. 5 and 6 will do for garancin, and are suitable for mixing with crystals or muriate of tin for forming a resist.

Red Liquors from Acetate of Lime.

		No. 7.	No. 8.
Acetate of lime liquor at 24° Tw., gallons	 	50	90
Alum, lbs	 	200	
Sulphate of alumina, lbs	 1 4		272
Ground chalk, lbs	 	12	34

On account of the cheapness of acetate of lime it is more used than acetate of lead. The above two red liquors are put together by first heating the acetate of lime liquor, in a copper boiler, to a temperature of 140° F.; then adding the alum or sulphate of alumina, and stirring until the lumps have disappeared; and lastly, the chalk is added by small portions at a time, to avoid loss by effervescence. The whole is then well stirred until nearly cold, allowed to settle, the clear drawn off, and the bottoms drained upon a woollen filter and washed with water until the washings fall as low as 2° Tw., when they are not worth washing any more. The red liquor No. 7, used at 20° Tw., gives the darkest red obtainable on calico for madder and garancin; the No. 8 liquor, at 16° Tw., is used for resist reds, and for mixing with iron liquor (iron mordants, about which more below) to produce chocolates for garancin work, and also is reduced for light reds. These two liquors are quite sufficient for the ordinary run of madder and garancin work.

Red Liquors for Madder Pink (Rose-colour).

		,		,	
	No. 9.	No. 10.	No. 11.	No. 12.	No. 13.
Water, gallons	41/2	I	20	3	60
Alum, lbs	16	3 ½	75	13	125
Acetate of lead, lbs	12	21	103	_	100
Acetate of lime (dry), lbs		_	30	-	-
Ground chalk, lbs		-	5		-
Common salt, lbs		-	IO		-
Nitrate of zinc solution at 15° Tv	v		_	1	_

No. 9 is for dark and No. 10 for light pink, being reduced or diluted when used with 3 parts of water to 1 part of liquor; No. 11 is excellent, for the reason that the addition of common salt has the effect of causing the mordant to attract moisture, and thus improve the ageing. The nitrate of zinc in No. 12 has a still stronger attraction for water, but should be added after thickening and when the liquor is cold, since this salt otherwise causes the starch and flour to run thin if boiled with them. No. 13 is only for reducing for light pinks (rose-colour), and will not give a good dark pink.

We now direct our attention to the mordants used to produce, with madder and its preparations, blacks, purples, and lilacs. The basis for these is hydrated peroxide of iron, or a basic insoluble salt of iron. We have already observed that the substance just named is used as a colour by itself, for producing nankin, rust, and chamois colours; but the quantity of hydrated oxide of iron required to yield with madder pigments the utmost effect is too small to produce by itself any colour upon the fabric.

The means employed to fix peroxide of iron upon tissues are—(1), the use of basic salts of peroxide of iron, which give up a portion of the oxide as a consequence of the capillary attraction of the fibre; (2), the use of certain neutral salts of peroxide of iron, the oxide of which can be precipitated by the employment of ammonia, caustic or carbonated alkalies, and some alkaline salts (e.g., phosphates, arseniates) the acid of which forms, with the peroxide of iron, insoluble compounds; (3), those salts of the peroxide of iron which are spontaneously decomposed by the volatility of the acid, while the base is set free; (4), the use of protoxide salts of iron, which, however, require higher oxidation simultaneously with or after the transferring of the oxide to the fibre; (5), lastly, the alkaline solutions of peroxide of iron. While enumerating all these possible means, we should also state that only one among them has been and is actually used, and after a lengthened experience has been found the best, viz., the proto-acetate of iron, or, as it is technically called, pyrolignite of iron. These preparations, after having been printed on, and after ageing, become changed, lose a portion or the whole of their acetic acid, and take up oxygen, with the result that there is deposited on the cloth an insoluble hydrated peroxide of iron, or at least an insoluble subacetate of peroxide of iron. It must be here remembered that, according to some authorities, the intermediate or magnetic oxide of iron is actually formed on the cloth, and is more efficient as a mordant than the peroxide. The tarry and other organic matters in ordinary iron-liquor have a decided effect in retarding the peroxidation of the protoxide present.

M. H. Schlumberger finds that good results may be obtained by the application of aceto-ferruginous solutions obtained by-(1), double decomposition between acetate of lead and sulphate of iron (green vitriol, copperas); (2), by acetic acid and iron (viz., the slow solution of scrap iron in crude acetic acid); (3), solution of iron in Bourgogne vinegar; (4), solution of iron in purified pyroligneous acid; (5), solution of iron in purified pyroligneous acid, and boiling for five minutes; (6), solution of iron in crude pyroligneous acid; (7), by double decomposition between protosulphate of iron and pyrolignite of lime. Before being applied to cloth as a mordant, these solutions ought to contain the iron in the state of protoxide: it is clear that the peroxidation of these liquids has to be guarded against as much as possible, because if it takes place the mordants no longer combine with the fabric, and that which may adhere is very readily removed by the subsequent cleansing and dunging. The effects of oxidation are especially injurious with blockwork, where frequently a small portion of mordant remains exposed over a large extent of surface to the action of the air. This change is far less perceptible in machine work. The nature of the thickening substance exerts a very great influence upon the fixation of oxide of iron. All things considered, starch fixes more of the oxide of iron than British gum, and the latter more than gum Senegal. The degree of viscosity of the mordant also greatly influences the result, and it is hence necessary to give to every mordant that proper degree of thickness which is required by the character of the design. The purified

pyrolignite of iron is prepared with pyroligneous acid deprived by distillation of the greater part of the tarry matters, and is of a strength of 10° Baumé, = sp. gr. 1'075.

The following mordants are for purples thickened with British gum :-

	PURPLE 8.	PURPLE 32.
Boiling water	48 litres	48 litres
Pyrolignite of iron at 10° Baumé	6 ,,	I 1 ,,
British gum	36 kilos.	30 kilos.
Oil of turpentine	375 grms.	375 grms.

Purple 10.—2 parts of purple 32 and 22 parts of purple 8. Purple 12.—4 parts of purple 32 and 20 parts of purple 8. Purple 16.—8 parts of purple 32 and 16 parts of purple 8.

FOR BLACK :-

Pyrolignite of iron at 10° Baumé .			 	32 litres
Calcined starch			 	10 kilos.
Water				
Quercitron liquor at 18° Baumé (sp	. gr. 1.1	43)	 	2 ,,
Logwood decoction at 17° Baumé (sp. gr. 1	1.134)		2 ,,
Olive oil				4 litre.

In former times it was the custom to add to the black mordant destined for block printing a salt of copper, chiefly the acetate, probably for aiding the ready combination of the oxide of iron with the cloth. Since M. Schlumberger observed that arsenite of copper and lime (15 grms. of each for r litre of mordant) has the effect of very particularly favouring the combination of oxide of iron with the cloth, it became the custom to add to mordants for purple a preparation known as the copper solution for purples, prepared with—

Lime water							
White arsenic	(arse	niou	is ac	id)	 	 	 750 grms.
Sulphate of co	pper				 	 	 750

The whole is boiled, and allowed to settle before being used. The use of this copper solution for purple mordant has been dispensed with, because its utility was not quite proved. The action of salts of copper in these mordants is chiefly beneficial with pure solutions of per-salts of iron, and especially when the mordants are thickened with gum Senegal. When other thickeners are used, and other solutions of iron, the pyrolignite for instance, there is no perceptible advantage in the use of a copper solution.

The mordant for purples known in this country as iron liquor, or black liquor, is made by steeping old iron of all sorts—such as hoops, worn out timplate, &c.—in warmed wood vinegar, or pyroligneous acid, obtained by the destructive distillation of wood. By continually moving the acid, and keeping up a moderate heat, it becomes saturated with iron in a few days, crude acetate of iron being formed. The iron liquor is met with in commerce as a fluid black by reflected light, but in thinner layers it is seen to possess a greenish-olive colour. Its taste is inky, and since the crude acid used in its preparation is not quite free from tarry matters the liquor has a peculiar smell. Its strength is from 18° to 28° Tw. (sp. gr. respectively 1'090 and 1'140).

Iron liquor at about 6° Tw. (sp. gr. 1.030) gives with madder, properly thickened (upon which much depends for the success of first-class styles of work), black; from 4° (sp. gr. 1.020) downwards to a very diluted state it gives

various shades of purple or lilac; mixed with red liquor it gives chocolates, of which more below.

Hyposulphite of iron can be used, according to M. Kopp's experiments, as a mordant for tissues, but the low price of the acetate will prevent the use of the first-named salt from becoming general. Hyposulphite of protoxide of iron, when exposed to the air, is slowly converted into protosulphate of iron, and lastly, into subsulphate of peroxide of iron, which is insoluble. Since this process of oxidation is very slow, the fixation of the peroxide, or sub-salt, upon the fibre is very intimate, and at the same time no perceptible weakening of the tissues takes place. The hyposulphite is prepared either by the action of sulphurous acid on the protosulphuret of iron suspended in water, or by the decomposition of the same sulphate by means of hyposulphite of lime, or by simply mixing hyposulphite of soda in crystals with a solution of sulphate of iron.

M. Persoz has proposed the use of an ammoniacal solution of pyrophosphate of iron. If this is printed on to the cloth, and slowly dried, it yields in the dye-beck, with madder, the most beautiful and pure purples and lilacs. Cloth mordanted with this solution can even be dyed in madder becks of madder already exhausted as far as other iron mordants are concerned.

Mordants for Browns and Chocolates.

These mordants are mixtures of those used for reds and for purples, and by simply varying the proportions of these two liquors very many modifications of tints may be produced. For simplicity's sake we call the undermentioned preparation for red (red liquor) Z in the after-mentioned compounds:—

Acetate of lead ,	
Water 20 litres.	
We designate as red mordant for brown the following mixture:	
Alum 144 kilos.	
Pyrolignite of lead 144 ,,	
Water 660 ,,	
Crystals of soda (carbonate of) 4 ,,	
With these the following brown mordants may be prepared:-	
A.—Mordant Z	tres
Pyrolignite of iron at 10° Baumé (sp. gr. 1.075) 4	93
Extract of quercitron at 20° Baumé (sp. gr. 1°162)	litre
White starch 2.5	kilos.
British gum 250	grms.
Gallipoli oil (huile tournante) 90	99
B.—Mordant for brown 12 litres 16	litres
Pyrolignite of iron at 10° Baumé 2 ,,	- 22
Extract of quercitron at 20° Baumé (sp. gr. 1.162)	litre 1
	kilos.
	grms.
	5 11

We cannot in this chapter enter into the mechanical details of printing on the mordants; it may suffice to say here that it is done chiefly by means of rollers

Plate V.



BLOCK-PRINTING.

The child to the right hand of the printer is the "tearer," whose business is to keep the colour equally spread out over the surface of the colour-box.

Sce page 472.



PAINTING IN RESERVES BY HAND.



made of copper, and upon which the design is engraved: as regards chintz and large patterns, these are obtained by what is termed block printing, wooden blocks being used containing the engravings of the patterns. Immediately after the cloth leaves the printing-machine it is dried by passing over metal plates heated by steam. By this operation acetic acid is volatilised, and a basic salt remains on the cloth. When block-printing has been resorted to, the drying takes place in a drying-room at a lower temperature than that just given, and consequently less acetic acid is volatilised. The fixation of the mordant is effected by two distinct operations, one of which, viz., the "ageing," has been described already. We add here the following particulars as regards the time required for the mordanted cloth to remain in the ageing room: for chocolates and browns, 72 hours; for purples and browns (another shade), 60 hours; for blacks and reds (if together), 48 hours; for pinks and reds, when not occurring along with other mordants, from 6 to 20 hours. It should be observed here, also, that proper ventilation must be kept up in the ageing rooms, since the presence of the vapours of acetic acid is injurious to the mordants, and since the admission of cold air to these rooms would condense the steam, and thereby spoil the goods: heated air is required for keeping up the ventilation.

We may quote here in full the researches made by M. H. Schiffert with the view of ascertaining the nature of the aluminous compound remaining on the tissues after drying and ageing: -(1). A piece of cotton, printed for foulards (a kind of handkerchief used in France for head-covers by women), and mordanted with acetate of alumina not containing any sulphate, was dried and submitted to the ageing process for several days; the cloth was next placed in a glass retort, and, after water and sulphuric acid had been added, distillation was performed. The result of this operation was that a perfectly neutral liquid was obtained, not containing even the slightest trace of acetic acid, which latter would have appeared if a basic acetate had remained on the cloth instead of hydrated alumina. (2). A piece of calico mordanted with alum, three-fourths of the sulphuric acid of which had been replaced by acetic acid from acetate of lead, was similarly dried and aged, and on being treated with cold water yielded sulphate of alumina. It hence follows that the acetate of lead had divided its action between the sulphates of alumina and potassa, both of which were present in the alum, while a portion of the alum had been left unacted upon. The tissue yielded, after being previously washed with water, on distillation with dilute sulphuric acid, not a trace of acetic acid. After washing, and next boiling with carbonate of soda, the resulting liquid did not contain sulphuric acid, which should have been present had there remained a subsulphate of alumina. Treated with hydrochloric acid, aided by heat, a large amount of alumina was obtained, precipitable by ammonia. (3). A piece of calico mordanted for ordinary red, dried, and aged for the usual length of time, did not on assay yield any acetic acid; treated with cold water it yielded a solution which became turbid by ebullition, throwing down a basic sulphate of alumina which can again serve as a mordant by being heated to 70° C. When a piece of this tissue was well and thoroughly washed with cold water it only retained hydrate of alumina, all the sulphuric acid being removed. The result of these experiments is, therefore, that fabrics mordanted with acetate of alumina do not retain, after drying and ageing, any acetic acid at all, not even in the state of basic acetate.

As regards the ordinary red mordant (red liquor), as generally made up, it appears that there remains a mixture of hydrate of alumina and neutral sulphate of that base. By treating the cloth upon which these substances are deposited with water, the neutral sulphate of alumina is dissolved, and while in solution reacts upon the hydrate of alumina, dissolves a portion thereof, and basic alum is again formed. The iron mordant is oxidised by the loss of acetic acid, and there remains a basic acetate of peroxide of iron.

The second portion of the process of fixing the mordants comprises the operations of clearing and dunging (dégommage, taking away the thickeners; bousage, from bouse de vache, treating with cow's dung). If the alumina and peroxide of iron were perfectly fixed on leaving the ageing-room, so that these substances were present in the fibre in an insoluble state, the only operation the goods would have to undergo previous to dyeing would be a washing in tepid water, in order thereby to remove the thickeners and other soluble substances which have served their purpose during the printing and are now of no further utility, and a thorough rinsing in fresh cold water. Experience has, however, taught that this simple operation is not sufficient, and does not yield in practice good results. We will illustrate this point by taking as example the ordinary red mordant, in the preparation of which only half of the sulphuric acid of the alum has been precipitated by acetate of lead.

M. Schiffert's experiments proving that the goods ready for the cleansing process contain alum and hydrate of alumina, what will happen when the pieces are washed in water? The alum will of course dissolve, and corrode, so to speak, a portion of the hydrate of alumina already fixed. This corrosion will be, it is quite clear, irregular,—that is to say, at one spot more, and at another less, of the hydrate of alumina will be eaten away, and, as a consequence, the depth and uniformity of the colours will suffer. The white portions of the pattern will, moreover, when brought into contact with a basic solution of alum, take up more or less of the basic sulphate of alumina, and will consequently attract colouring matters in the dye-beck. Something analogous will of course take place with regard to the iron mordants; though as yet incompletely fixed, subacetate of peroxide of iron will-on being brought into contact with water-become resolved into soluble neutral acetate and sesquioxide of iron, and the acetate rendered soluble will of course act as mordant upon the white portions of the pattern. All these effects are increased by the incomplete decomposition which the mordants undergo in some portions of the goods. Indeed, if the heat and moisture are not very regularly diffused over the whole ageing-room, it is possible that in some portions of the goods the mordants are not thoroughly aged, and have consequently retained a great deal of their solubility. Taking all this into consideration, it is quite clear that a simple washing, to dissolve thereby the thickeners, would lead to the production of spotted and irregular shades and to the staining of the white portions of the pattern. The manufacturers, dyers, and calico-printers have overcome these difficulties of the cleansing by substituting for water a tepid bath of cow-dung. Cow-dung contains mineral salts and insoluble organic matter, and by the joint action of these substances it causes the complete saturation of the mordant, the precipitation of the metallic oxides, and prevents the adhesion of any oxide which may become detached (mechanically loosened) or dissolved, to the white portions of the pattern. As a matter of course cow-dung is always plentifully mixed with the urine of the animal, and

contains a certain amount of phosphate of soda and of carbonate of ammonia. which probably play an essential part. The use of cow-dung is apparently of old origin, although on this subject no very precise data exist. It is known that the Swiss calico-printers and dyers made use of it in the middle of the eighteenth century, and M. J. Hausmann pointed out the benefits derived from this material in 1790.* M. D. Keechlin has set forth the favourable effects of the dunging in the following paragraphs+:-The aim to be attained by the use of cow-dung is (1), to effect the entire combination of the sub-salts of alumina with the fibre of the cloth, by causing the separation of nearly all the acetic acid which had not been volatilised during the drying of the mordant; (2), to dissolve and remove from the cloth a portion of the substances which had been used as thickeners; (3), to separate and remove from the fabric the uncombined portion of the mordant, and likewise to remove such particles thereof as are simply mechanically fixed by the thickeners; (4), to prevent, by the peculiar nature of the substances which constitute the dung, the fixing upon the white portions of the cloth of any non-combined mordant which becomes soluble by the acetic acid set free, and which acid at last accumulates in the dung-bath. As for the theory of the action of the dung, the clue must be sought in its composition. The labours of Morin, Perrot, § and Camille Keechlin have elucidated this question to a certain degree, without, however, solving the question completely. According to M. Morin, the filtered aqueous extract of cow-dung, after having been exhausted by alcohol and ether, yields to water a soluble principle which he has named bubuline, and which he considers to be the active constituent, because, according to his experiments, this material has the property of precipitating most of the solutions of metals: later researches have shown, however, that the bubuline has no separate existence as an immediate principle, being rather a mixture of albumenoid materials, coloured by compounds due to the bile, and of vegetable origin. According to M. Perrot, cow-dung from animals fed with dry fodder, contains in 100 parts-

Water 69	9.28
Bitter principle	0.72
Saccharine matter	0.03
Chlorophyll	0.28
Albumen	0.63
Lignine 20	5.99
Chloride of sodium	0.08
Sulphate of potassa	0.02
Sulphate of lime	0.22
Carbonate of lime	0.24
Phosphate of lime	0'46
Carbonate of iron	0.00
Silica	0.14
100	0.47

* Lettre à Berthollet, "Annales de Chimie," vol. xii., p. 111.

‡ "Bulletin de la Société Industrielle," vol. iv., p. 164.

§ Ibid., vol. viii., pp. 113 and 124.

^{† &}quot;Bulletin de la Société Industrielle," vol. i., p. 313. At the time this was written the ageing process, at least as now known and practised, was not used.

It would be interesting to re-examine this substance with the improved means of chemical analysis now at command. To the list of the salts quoted by M. Perrot must be added alkaline phosphates, which, to some extent, exist in all animal excrements. M. Perrot also observed that the soluble portion of the cow-dung yields in the cold an abundant precipitate with the red liquor, which increases when the fluid is heated. The insoluble portion of the dung retains, on being boiled with red liquor, a certain proportion of alumina. M. C. Keechlin has made some experiments with the contents of a dung-bath made up in the usual manner, and therefore containing 80 kilos, dung, with from 40 to 45 measures of water, temperature 70°, after there had been passed through it several pieces of cloth, mordanted for good black, fine red, and purple. The bath was not at all exhausted; on being left quietly standing the liquid did not become clear; there remained in suspension a black greenishcoloured matter, weighing 9.5 grms. for 25 litres of the liquid operated upon. The filtrate had a dirty yellow colour, was astringent, and so acid as to colour blue litmus-paper red. Normal dung is either quite neutral or alkaline. On being evaporated to dryness the liquid left 22.8 grms. residue. The previously suspended ligneous matter retained on the filter weighed, after, drying, about 28 grms. The incineration of these various substances yielded, on analysis, the following quantities of alumina and peroxide of iron:

Ligneous matter	o.18e gtm
Suspended matter (9-5 grms.) Alumina Peroxide of iron	0.665 ,,
Peroxide of iron	0'456 ,,
Soluble matter (22:08 grms.) { Alumina Peroxide of iron	0.660 ""
Peroxide of iron	0,000 33

It should be observed that the relatively small proportion of alumina contained in the aqueous extract could not be detected by any of the usual reagents, being consequently masked by the presence of organic matters. Add to this the fact that the aqueous extract of a dung-bath, after it has been used for the clearing of mordanted goods, contains invariably almost as much alumina as the insoluble portion, yet white calico is not mordanted on being immersed in this liquid, thus proving that the alumina is in an unusual condition. The same applies to the iron mordants. When to a freshly-made aqueous infusion of cow-dung gradually increased quantities of the acetates of iron and of alumina are added, it will be seen that the precipitation does not ensue immediately, but only appears when a certain limit is reached. There is thus good reason to suppose that cow-dung contains a soluble substance, probably of an albuminous nature, which possesses the property of preventing the precipitation of the alumina and oxide of iron by the usual reagents.

According to these results the influence of cow-dung in cleansing may be viewed in the following manner:—The first portions of the acetates of alumina and iron which are separated from the goods remain in solution, but cannot injure the white portions of the fabric, and this continues as long as the masking power of the organic compounds is not exhausted. At the moment of that exhaustion taking place a precipitation of the oxides ensues, in consequence of the action of the alkaline phosphates, and when at last this useful effect is also at an end all the portions of the mordant which become detached can attach themselves to the white portions of the goods. It is therefore

clear that the cow-dung owes its good effect to the fact that it contains substances capable of masking, or precipitating by means of double decomposition, the mordants which get detached. To the saturating effect of the alkaline phosphates contained in the dung is due its power of fixing upon the goods a larger proportion of the oxides than would be left by a simple cleansing with water. We should not overlook the utility of the insoluble substances suspended in water. These particles play a chemical as well as a mechanical part as regards the saturation due to phosphates and alkaline-earthy carbonates, and take up the alumino-ferric precipitates, thereby preventing them from becoming fixed to the white portions of the tissue.

Since in actual practice substitutes have been found for dung, chiefly of a saline nature,—e.g., the phosphates of soda and lime, silicate of soda and others, about which hereafter, all of which possess the power of saturating any as yet undecomposed mordant, while they also act as precipitants for any portions which may become detached,—we have, by analogy, a right to attribute to the phosphates contained in the dung an active part.

The dung-bath is commonly made up of 30 litres of cow-dung to from 1600 to 2000 litres of water: dung from animals fed upon green forage, and especially upon beet-roots, is less useful and advantageous than the dung excreted by animals fed with dry fodder. Powdered chalk is usually added to the cowdung-bath, especially for acid mordants and heavy patterns. It should be noted that the mordants acquire in the dung-bath a peculiar olive-green colour. This appears to be a true dyeing process, chlorophyll and some of the bile pigments being deposited. It is difficult to state the number of pieces of goods which can be passed through a given bulk of such a bath with good effect. The number depends on the acidity of the mordants and the nature of the designs, and therewith varies from 20 to 60. The duration of the immersion has to be modified according to the concentration of the mordants and the kind of thickening used, and these considerations also regulate the temperature to be applied. When starch or farina has been used the temperature should be higher than when gum is employed. It varies from 45° to 100° C. Some kinds of prints, especially if starch or farina have been used as thickeners, require two dungings and a washing between. A strong and acid mordant is more difficult to dung and cleanse well than a neutral mordant, and this applies especially for madder work. A too high temperature and a too large quantity of dung are injurious to weak mordants, and especially to rose-reds and pinks.

Great care is required in passing the goods, regularly stretched and without folds or creases, and also as rapidly as possible, through the dung-bath, because from the moment the hot water penetrates the cloth the acetic acid leaves it, and therefore if the immersion took place slowly, and fold by fold, the acid and the uncombined mordant would spread and have time enough left to dissolve the alumina which had already combined, the consequence of which would be inequality and deterioration of the tints to be afterwards brought out in the dye-beck. After leaving the dung-bath the goods are several times thoroughly washed, in order thereby to eliminate the last portions of the thickeners.

Among the many substitutes for dung we enumerate the following:—the double phosphate of soda and lime, the arsenites and arseniates of soda, and the silicates of soda. These have lattely almost entirely displaced cow-dung.

The mordanted and aged cloth is passed into weak and hot solutions of the above-named substances, with the view of fixing thoroughly the mordant in the cloth and removing any excess that may have been used, without allowing it to fix itself on the white parts. By the introduction of these dung-substitutes and improved vats a great saving of time, labour, and expense has been effected. On the Continent bran is also used as a substitute for dung. It contains a large amount of alkaline and alkalino-earthy phosphates, while, moreover, the ligneous particles and other organic matters insoluble in water give this substance some resemblance to dung in its mechanical action. It has the great advantage of not containing colouring matters, and is therefore, for light shades, preferable to dung. From 50 to 60 litres of bran are used to some 3000 litres of water. The salt known as dung-substitute, chiefly made and used in this country, is either phosphate of soda and lime or the arseniate of these bases. From 50 to 80 grms, to the hectolitre of water are used.

There is a difference of opinion as regards the good results obtained by these substitutes; experience proves that in the case of the best dung substitutes a final turn in cow-dung before dyeing is advantageous, it being better for the mordanting oxide that it should go into the beck in a partly saturated state than in a state of the highest activity. In a majority of cases the colours will be more solid, brighter, and faster when the combination between the mordant and the colouring matter is slow and gradual than when it is rapid. Generally we may state, that with the same mordant, the dung substitute gives rise to the production in the dye-beck of far deeper shades of colour than when cow-dung is used. This is readily explained by the more complete saturation of the mordants, when the substitute is used, and the consequently smaller proportion of mordant detached from the cloth. The following substitutes for finishing off the fixation of the mordants have been proposed:--Ammoniacal gas (M. Wessorling) for purples, alkaline bicarbonates, silicate of soda. This last substance has almost entirely taken the place of dung, and since experience teaches more and more the precise conditions how and where to apply it, it has even come into use where its utility was most doubtful. Its mode of action is essentially saturating; it fixes all the alumina of the mordant by causing its precipitation in and on the fibre before it has time to become detached. The following brief description of the mode of applying the silicate in madder work will give the reader some idea of its use, with the observation that the prescriptions in this instance, and likewise as regards all mordants and other matters of this kind, although they be fit for actual use on the large scale, are not to be considered as given for practice, it being a well-known fact that every manufacturer has to consider his own peculiar arrangements and situation as well as the style of work he cultivates. The goods pass in two minutes' time through two troughs or tanks, the contents of which are heated to 50° = 122° F., and each containing for goods mordanted for brown and red, black and red, brown only, red only, and rose upon a white ground-2800 litres of water and 85 litres of silicate of soda at 10° B. (sp. gr. 1.075). When only mordanted for purple and black, black only, and purple only, the contents of the tank are-2800 litres of water and 60 litres of silicate of soda of the above-named strength. If it happen that by this treatment the colours are too deep after dyeing (a small pattern may be easily tried, of course, in the dye-beck), the goods should be dunged

a second time, using 36 litres of dung for 900 metres length of cloth, leaving it for half an hour in the bath at a temperature of from 38° to 57° C.

The following example of the dunging of cloth for garancin work will give an idea of the actual operation as performed on the large scale and the ingredients employed. Goods for garancin work are, after leaving the ageing room, twice dunged;* for blacks, violets, purples, greys, catechu browns, reds, and puce browns the first dunging consists in passing the goods successively in two minutes' time through three tanks provided with rollers, and containing:-First tank-Water, 1400 litres; chalk, 12.5 kilos.; cowdung, 40 kilos. heated to 38° C. Second and third tank-Water, 2800 litres; cow-dung, 35 kilos.; quercitron, 11 to 14 kilos., heated to about 82°. The second dunging is performed in one tank large enough to hold 12 pieces of cloth at a time; it is left in the tank and its contents for half an hour at a temperature of about 63°. The tank contains:—Water, 1200 litres; dung, 20 kilos.; quercitron, 6 kilos.; sumach, 2 kilos. For brown only, black only, grey and brown together only, red and black together only, brown and black together only, brown and catechu brown together only, brown and purple together only, the first dunging is performed in three tanks with rollers containing:-No. I-Water, 1400 litres; cow-dung, 30 kilos.; chalk, 10 kilos., heated together to 38°. Nos. 2 and 3-Water, 2800 litres; cow-dung, 25 kilos.; quercitron, 23.05 kilos., heated to 82° C. The second dunging for these colours is performed also in a tank capable of containing 12 pieces of cloth at once, the charge being: - Water, 1200 litres; cow-dung, 25 kilos.; quercitron, 10 kilos. The whole is heated to 74°, and the goods are left for half an hour. For brown and purples only a little less quercitron is taken. For garancin work the dunging may also be replaced by the use of silicate of soda, but in that case the colours require a stronger chlorine treatment, about which more below. The use of a sal-ammoniac bath instead of dunging is only suitable when aluminate of soda has been used as a mordant.

We now have to treat of the operation of dyeing with madder, an operation which requires, when performed on the large scale, very great and special care, and a very intimate knowledge of the conditions essential to obtain the fullest, brightest, most uniform, and fastest colours, while simultaneously the fullest utilisation and greatest possible exhaustion of the colouring matter of the dye-stuff has to be secured. On the small scale it is easy enough to dye with madder a piece of previously mordanted and dunged cloth, since it is only necessary to keep the pattern (say I foot square) fully immersed in a bath made up of 12 grms. of madder and 1 litre of water, while the temperature is slowly raised to the boiling-point during the lapse of one hour's time, care being taken to stir the mixture frequently in order to insure uniformity of the colour. The colouring matters of the madder, while gradually dissolving in the liquid contents of the dye-beck, combine with the mordants, forming coloured lakes, the shade of which as well as the intensity depends upon the quality and quantity of the metallic oxide fixed to the cloth. When it is desired to obtain on the large scale a certain shade of constant intensity (depth) the printer or dyer has to take into account a great number of conditions which influence the desired result. Among these, for instance,

^{*} Some printers dung all goods twice; first in what is called the "Dolly," and then at a higher temperature in the dung-beck.

the composition of the water employed and the peculiar nature and richness of the dyeing material are prominent. All the different kinds of madder met with in commerce do not act in the same way in the dye-beck, and even when of the same origin its behaviour may be influenced by natural causes, good or bad season, for instance, during its growth, or by adulteration. To this we must add that the different commercial preparations of madder (fleur de garance, garancin, &c.) each yield results peculiar to themselves, and it will be clear that each of these substances requires a specially modified treatment in the dyeing operation.

From these few observations it will be readily understood that a manufacturer has first and foremost rigorously to study, and next bring into practice, the most suitable conditions for the duration of the immersion of the cloth, the temperature to be given to the contents of the dye-beck, the mode of heating, &c.

Before we review each of these conditions separately, we may yet mention the following generalities:—The art of madder dyeing (French, garançage) has been, indeed, in our days brought to so high a degree of perfection, that it is difficult to think that it can be further improved. We can daily admire the beautiful execution of tissues, perfectly got up, where upon a ground of dazzling whiteness there are designs in rose-red, red, lilac, violet, brown, or black tints, and shades of the utmost brilliancy, and, moreover, so fast as to admit of strong and repeated washing. These results have been obtained by the joint efforts of the many intelligent men who have devoted their time and capital to this branch of industry. The introduction of resin soap in the bleaching process has rendered the getting up of white grounds after the dyeing process far more readily obtainable. A better and more intimate knowledge of the mordants and the processes for fixing the same, the substitution of the silicate of soda for cow-dung in many cases, have all contributed to a more regular and more complete fixing of the metallic oxides (mordants), and hence to better results; the dyeing process has been greatly benefitted by the introduction of those madder products known as fleur de garance, garancin, commercial alizarin, &c. Lastly, the clearing (avivage) has become a more speedy and far more manageable operation by the skilful application of chemicals. All practical dyers agree herein, that the dyeing operations with fleur de garance, garancin, and similar products require less care and are far more easily executed than that with madder, and therefore we will turn our attention first to the latter substance, quoting succinctly the results of the remarkable researches and labours of M. H. Schlumberger* on this subject, who fully investigated one by one each of the conditions most favourable to obtain good results.

First, as a necessary condition it should be borne in mind that the cloth to be dyed should be thoroughly well prepared in every respect, well cleared, and its mordants well fixed. As to the duration of the madder dyeing, the goods may be left in the dye-beck for six hours without fear of deterioration of the colours produced, but since labour, fuel for heating, and loss of time are important matters, and since it is a well-known fact than an equally good result can be obtained in less time and with a decided gain in many respects, we may state that four hours is sufficient to all intents and

^{* &}quot;Bulletin de la Société Industrielle de Mulhouse," vol. viii., p. 327.

purposes when a boiling temperature is kept up for the last thirty minutes of that period. It has been found that when the goods are left in the dyebeck for eight hours at 50° C., more colouring matter has been extracted (the madder more exhausted) than when the fabrics are only kept in the beck for three hours and ebullition resorted to. This observation applies to Alsace as well as to Avignon madder. When the dyeing process is continued for more than six hours the colours produced stand clearing* (avivage) less well than when the time has been shorter. Since the quantity of water is of considerable influence, this point was particularly investigated by M. Schlumberger, and as result of his researches he concluded that I part of madder to 80 of water was the best. When less water is taken, say 20 parts to I part of the madder the colours produced are less fast. We have to observe here, however, that on the large scale these proportions are not rigorously adhered to, and that in order to save the cost of fuel and the number as well as the size of dye-becks more concentrated baths than I to 80 are used.

As regards the quality of water we have, in this instance, chiefly to consider the effects of the lime salts it may contain, and especially the carbonate of that base. Taking Alsace madder as an example, that substance is acid, and requires, in order to produce fast colours, the addition of some chalk to the water in the dye-beck. Hence a calcareous water will not give rise to any perceptible loss of colouring matter, but if Avignon madder be used, a substance of which we know already that it contains a certain quantity of carbonate of lime, any addition thereto to the water used for dyeing will certainly cause a serious loss of dye material. It is clear, therefore, that in localities where the water at hand may happen to contain lime salts (carbonate or sulphate) to any large extent it will be best to purify it by convenient means or to use for filling the dye-becks the condensed steam from the boilers.† According to M. Schlumberger it is best to heat the contents of the dye-beck to 60° before the goods are entered, but on the large scale this arrangement would cause irregularities in the dyeing, since at that temperature the activity of the bath is already considerable, and, moreover, experience has proved that the shades obtained by immersing the fabrics in the bath at a too high initial temperature do not stand clearing so well as when entered at lower temperatures, viz., 20°, 30, or 40°. There is some difference of opinion as regards the highest temperature to be applied in order to utilise all the colouring matter. According to some persons the temperature should be raised to the boiling-point, but according to the author just named a temperature of 50° for Avignon madder and 80° for Alsace exhausts these substances as completely as a temperature of 95°, provided the dyeing be prolonged for eight hours. Although a boiling heat favours the fixation of the

^{*} There is, unfortunately, too close a similarity in the English words cleansing and clearing, and for that reason we have added (avivage); be it understood that cleansing is an operation which takes place before the dyeing process, and is named in French degommage and bousage; though the latter term, as can be inferred from our foregoing pages, rather applies to dunging, clearing (avivage) is an operation which takes place after dyeing, and is chiefly intended—(1) for the washing away of dirt and superfluous colouring matter; (2) for bringing out the peculiar brilliancy of the colours. The process of clearing will be fully detailed after we have described the dyeing.

⁺ Since in printing works, just as in sugar refineries, much steam is used for heating purposes, and circulates in piping, it is not difficult to collect a sufficient quantity of pure water.

colouring matter, the brilliancy and beauty of the shades produced are somewhat impaired, whence this maximum of temperature is often avoided in practice. It is of the very utmost importance to keep the temperature of the bath gradually and steadily rising, and to guard especially against a fall of the heat, which is invariably attended with great loss of colouring matter. For instance, if the temperature has been raised to 55°, then cooled down to 30°, again heated up to 70°, next again cooled to 40°, and then brought up again to ebullition, there will ensue a loss of 40 per cent. The explanation of this phenomenon is not easy, but since this phenomenon is not observed with fleur de garance and garancin it is evident that the soluble constituents of the madder play an active part in the process going on in the dye-beck. The steeping of madder in water previous to use is injurious, and invariably gives rise to loss of colour, not because it is thereby destroyed, since it can even resist fermentation and a far advanced stage of putrefaction, but the colouring matter becomes masked. When Avignon madder is thoroughly mixed with a quantity of ice-cold water at oo (32° F.) and the mixture filtered, a deep brown filtrate is obtained, which, when heated in the usual manner, dyes a previously mordanted piece of calico very well; but if this experiment be repeated with water at 30°, the filtrate is quite clear and does not yield any dye. If Alsace madder is treated in the same way it yields at oo and at 30° solutions equally rich in colouring matter and fit for dyeing.

We quote here the results of some experiments made in this direction:—
46 grms, each of the above kinds of madder were steeped for fifteen minutes
in 32 times their weight of distilled water, and next filtered with the following
results:—

caurta.		
	Avignon madder.	Alsace madder.
At oo dyed as well as if }	6 grms. of the material were used.	9 grms. of the material were used.
The residue on the filter dyed as if	30 grms. were used.	Owner
Loss	10 grms.	Married P.
At 30° dyed as well as if	I grm. of the material was used.	5 grms. of the material were used.
The residue on the filter dyed as if	28 grms. were used.	
Loss	17 grms.	_

These figures can be interpreted in the following manner:—The colouring glucosides of the Avignon madder, which is neutral or alkaline, are, for a short time at least, not acted upon and preserved intact at o°, but are rapidly split up at 30° into an insoluble colouring matter; since Alsace madder is acid this decomposition is not so rapid, and consequently the phenomena produced are less sharply defined; this observation applies to Zealand madder, which is also acid. If the question be asked, what quantity of madder or any of its commercial preparations should be used in the dye-beck, our answer is, that it is difficult, if not impossible, to fix constant rules. Something depends upon the greater or less fulness of the designs executed upon the cloth, upon the greater or less degree of penetration of the mordant into the fibre, the greater or less perfection of the ageing and fixing, the perfection also of the original bleaching of the cloth, and, lastly, the greater or less strength of the mordants applied. All these points influence the quantity of dye-stuff required. As a

general rule it should be observed that the mordants ought to be saturated, and since the shade desired is dependent upon the strength of the mordants applied, it is evident that this condition will influence the quantity of madder required. When the mordants are used too strong and their full saturation not obtained (that is to say, plenty of dye-stuff present in excess), there is a great risk of inequalities arising in the results. The best way to fulfil all requirements is to have sample patterns printed in stripes with the identical mordants applied to the goods attached to them when immersed in the dyebeck, and therefore simultaneously dyed, and to use the results as a guide to the proper quantity of dye-stuff.

According to M. H. Schlumberger's researches, mordants may within certain limits be supersaturated by an excess of madder without impairing thereby the brightness of the shades, provided care be taken to adjust the quantity of the water in the dye-beck in due proportion to the madder. If this is not properly regulated after clearing the shades obtained are spotted, unequal, and dull. Contact of air does not interfere. The materials of which the dvebecks are constructed exercise a great influence on the results when the heating is effected by means of open fire or by a water-bath, but with the application of steam the material becomes of no importance whatever. When metal-made dye-becks are used heated by open fire or a water-bath it very frequently happens that a loss of some 40 per cent of dye material is experienced, but this decrease is not observed when steam is used, and is, moreover, only observed with madder, not with garancin or any other of its commercial derivatives, and the loss is therefore due to the unequal influence exercised by the soluble particles of the madder. As a general rule it may be said that the addition of various substances to the dye-beck along with the madder in order to increase its tinctorial power, and to attract a larger proportion of its active principles, has never yielded favourable results.

In the paper published by M. H. Schlumberger,* and reproduced by M. J. Persoz in his celebrated work "Traité de L'impression,"† will be found a long list of substances drawn up by a German chemist, with the view of showing the value of a large number of substances used as additions to the madderbath. It is needless to enter into further details on this subject, since experience has proved the uselessness of such additions, none of which, moreover, have any scientific interest.

We must not, however, neglect to notice the favourable effect of a certain quantity of oxalate of ammonia as an addition to the dye-beck when madder is employed, as first observed by M. E. Schwartz. The addition of this salt gives rise, in all probability, to a double decomposition ensuing between it and the lime salts of an organic as well as of organic acids contained in the madder. The colouring matter combined with these salts is thus set free, while the oxalic acid seizes upon the lime. The addition of alkalies or chalk may or may not be useful according to the proportion thereof employed, and the nature of the madder worked with. Since Alsace and Zealand madder are both acid, the former, however, far more so than the latter, and contain

^{* &}quot;Bulletin de la Société Industrielle de Mulhouse," vol. viii., pp. 293 to 360.

⁺ Persoz, "Traité de L'impression des Tissus," vol. ii., p. 503 and following.

[‡] We need scarcely remark that to add oxalate of ammonia along with chalk is a mere waste of materials. Where either of these substances is beneficial the other is likely to be injurious.

only a small quantity of calcareous matters, alkalies or chalk may be within reasonable limits advantageously added to the contents of the dye-beck. As regards the first-named kind, it is a known fact that it will not produce fast colours without this addition.

As to the part played by chalk in madder dyeing, there can be no question whatever about the advantage resulting from its addition, since on this point the comparative experiments made by M. H. Schlumberger with Alsace madder, with or without chalk, and with Avignon madder, which is naturally rich in lime compounds, are incontestible. Zealand madder has been experimented with some years ago, comparatively with Avignon madder in a similar manner, by a committee of practical and scientific men,* care being taken (a matter of importance in such trials) to use madder of the same age and maturity in both instances, while the water used was either distilled or water the solid contents of which were perfectly known. The results obtained on the large scale have proved that Zealand madder of proper maturity does not absolutely require the addition of chalk, but with that addition the shades produced are superior, the mordants and all conditions being alike, to those yielded by Avignon madder or any other. This fact has also been observed by Prof. Girardin, who along with very many in France regret that, in order to please the Vaucluse madder growers, Zealand madder is practically prohibited from importation by an enormously high rate of duty. As to the mode of action of chalk, this may be either simply for saturating the acidity of the madder, or it may actually enter into the lake to be produced, and thus render the colours fast. We have already said that Alsace madder does not vield shades which stand clearing well unless chalk has been added. If the saturation of the acid were the only object, it is quite clear that the precise quantity required for neutralisation of the acid would suffice, but this hypothesis is not in accordance with the actual results obtained by experience on the large scale, which have conclusively taught that an excess of chalk is absolutely necessary. Experiments made by M. D. Koechlin many years ago proved that dyeing operations made with a binary mordant give rise to the production of faster colours than when only a single mordant is used. M. H. Schlumberger's opinion on this point is, that the chalk becomes fixed on the mordanted portions, producing a binary compound of greater stability than that of the aluminous substance by itself only.

The following may illustrate the meaning here briefly expressed:—When a piece of cloth is first mordanted with a preparation of binoxide of tin, next with an aluminous mordant, and next treated with an acid in order to discharge again the mordants previously applied in some parts of the cloth, it will be seen that after the cleansing, washing, madder dyeing, and clearing operations the discharge material, acid in this case, has readily corroded the aluminous mordant, and also readily enough the tin mordant wherever these two were applied singly, but in all portions of the cloth where the two mordants are placed upon each other no such discharging action has taken place. On leaving the dye-beck the colours produced, wherever the two mordants come together, are as intense and deep as if no acid had ever been

^{*} Among them M. H. Schlumberger, jun., M. Prévinaire, M. Pincoffs, M. Salomonson, Professor Van der Boon Mesch, and others. These experiments were made at Haarlem, at Enschede, and partly also at Rotterdam and Ghent.

applied as a discharge at all. The eye of an inexperienced observer in these matters cannot fail to detect that, after the cloth has been thoroughly cleared, the shades given by the alumino-stannic mordant are far deeper and far faster than those yielded by each of them separately. As a further proof of the effect of the two mordants together, the clearing operation (avivage) may be so far pushed as to lead to the partial destruction of the colours of each of the mordants singly, whilst those of the compound mordant will be found to have resisted this energetic action. The following results of experiments confirmatory of M. Schlumberger's opinion may be useful here:—A piece of white calico was taken and mordanted with acetate of alumina, the mordant was fixed and dunged, a portion was dyed with Avignon and another portion with Alsace madder, and cleared. After this the pieces were cut up into swatches of 50 square centimetres, and these were incinerated with proper precautions. In the ash the amounts of lime and alumina were quantitatively estimated, leading to the undermentioned results:—

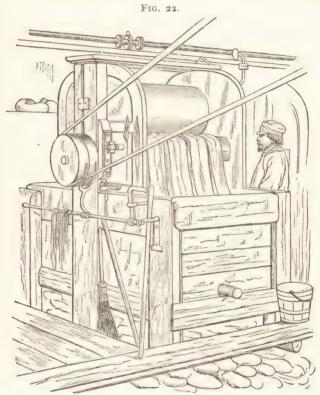
		Quantities by weight in grammes,	
		Lime.	Alumina
χ.	White cotton without any preparation but bleaching	0.01	
2.	White cotton as above, but passed through chalk- milk of the same strength as that used in the dye- beck, and next washed in water very slightly acidulated with acetic acid	o.oi	
3.	Mordanted and cleansed cloth	0.002	1.25
4.	The same dyed with Alsace madder	0.00	1.27
5.	The same as No. 4, but cleared	0.02	0'42
6.	Mordanted and cleansed cloth dyed with Avignon madder	0.53	1.58
	The same as No. 6, but cleared	,	0.51
0.	Alsace madder, with the addition of one-sixth of its weight of chalk in the beck	1	1.59
9.	The same as No. 8, but cleared	0.50	0.52
IO.	The same as No. 2 above, but experiment repeated	0.002	. —

We learn, from the above-quoted results, that white unmordanted calico as well as the mordanted material does not retain chalk by being passed through chalk-milk, or at least does not contain any of that material after being washed in water slightly acidulated with acetic acid; but it is different during the dyeing process, and after the clearing process the relation of the alumina to the lime is 2 atoms of alumina for 3 atoms of lime.* During the dyeing process there is dissolved alizarate of lime, which combines with the mordanted portions of the tissue. The clearing process takes away the lime, and still more of the alumina, but leaves a definite compound of alizarin, lime, and alumina. The analysis of the dyes obtained with oxide of iron as base

^{*} In the opinion of many competent authorities there is little foundation for the view that chalk adds to the fastness of madder colours, by forming a triple compound of colour, alumina, and lime. In using pure alizarin the smallest quantity of lime acts injuriously, by diminishing the strength of the colour. In crude madder there are not merely acids, but other colouring matters, which combine with the lime and allow the alizarin to produce its full effect.

has also resulted in the detection of the existence of a combination of the mordant and lime with the colouring matter, viz., if madder had been used containing calcareous matters naturally, or if chalk had been added in the dye-beck.

All these observations refer to madder only. As regards fleur de garance and garancin, irregularities in the mode of heating, the material used in the construction of the dye-beck, and many other conditions, have no prejudicial action upon the process of dyeing. Generally speaking fleur de garance can be used instead of madder in all cases where clearing is required, but madder is preferable for the kind known as triple pink (rose-red); fleur de garance,



again, is suitable for purples and blacks; for red and black a mixture of fleur and madder is used, which yields a deeper black than fleur by itself.

On the large scale madder dyeing is performed in well-constructed, water-tight, wooden tanks, heated by steam, and provided with properly contrived rollers moved by means of straps so as to impart to the goods stretched on these rollers a suitable motion, and thereby to cause a regular renovation of the points of contact between the bath and the cloth. Fig. 22 will give the reader some idea of this contrivance, which is also in use for the dunging, branning, and soaping processes. As regards the practical

execution of madder dyeing, it is of course evident that the details vary in different works within certain limits, and therefore the undermentioned figures have no absolute value, but may serve to illustrate the operation, while it should be at the same time understood that the strict observance of the underquoted prescriptions yields excellent results on the large scale.

A. Ordinary Madder Style Work.

The previously mordanted and cleansed goods are washed in the washingmachine for half an hour.

No. 1. White ground, with red and black designs:—For goo metres of cloth—g pieces, each 100 metres in length (100 metres are equal to 109'363 yards), are dyed at the same time—10 kilos. of fleur de garance; 10 kilos. of madder; 1200 litres of water. The temperature should be regularly raised from 19° to 82° during two hours, and be kept for half an hour at the highest point. If the pattern is heavy (that is to say, one which leaves little white) the weights of madder and fleur should be each 25 kilos. for the same amount of water.

No. 2. White ground, with a light design, puce-coloured:—900 metres of cloth: 7.5 kilos. of fleur de garance; 7.5 kilos. of madder; 1200 litres of water. The temperature to be raised in two hours from 38° to 82°.

No. 3. Puce and red; a heavier pattern upon a white ground:—goo metres of cloth: 20 kilos. of fleur de garance and 20 kilos. of madder; and again 1200 litres of water. The temperature should be raised in two hours (that is to say, the dyeing process performed during that time), the temperature being regulated from 38° to 82°.

No. 4. White ground with a pink design:—900 metres of cloth: 35 kilos. of madder and 1200 litres of water. The dyeing process to last three hours, the temperature being raised gradually during that time from 38° to 75°.

No. 5. White ground with a deep pink pattern:—900 metres of cloth: 25 kilos. of madder; 1200 litres of water. Dyeing process and temperature as with No. 4.

No. 6. Rose-red pattern upon pink ground:—900 metres of cloth: 72 kilos. of madder; 1200 litres of water. Dyeing process and temperature as indicated under No. 4.

No. 7. Lilac and black pattern upon a white ground, the colours of the pattern not very deep:—cloth, 900 metres: madder, 15 kilos.; fleur de garance, 15 kilos.; water, 1200 litres. The dyeing process to last two hours, and the temperature to be gradually raised from 38° to 88°.

No. 8. Lilac and black pattern upon white ground, the design being moderately heavy. It will be quite clear to any one who takes the trouble to inspect a few hundred samples of variously printed cloths, in madder styles, that there must, as regards the quantity of madder to be used, exist a relation between that quantity and the quantity of mordant, which of course depends upon the extent of the design in relation to the white ground left. Cloth, goo metres: 16 kilos. of fleur and 16 of madder, with 1200 litres of water, and the dyeing process and temperature as in No. 7.

Since a higher temperature has the effect of rendering the reds a bad colour, pieces containing red designs are never heated higher than 82°, and preferably even less. It should be observed here, also, that instead of madder, or a

mixture of madder and fleur de garance, the latter may be used alone, it being borne in mind that its tinctorial value is twice as great as that of madder.

B. Garancin Style.

When garancin is used it is frequently mixed with a larger or smaller quantity of lima and sapan woods, and also sumach. Patterns containing much brown remain in the dye-beck or tank for two hours; while those wherein red, lilac, purple, grey-black, and catechu-brown predominate remain two and a half hours.

For 12 pieces of cloth, at 100 metres each, with a full pattern, the following ingredients are taken:—Water, 1200 litres; garancin, 12 kilos.; lima wood, 6 kilos.; quercitron, 2.5 kilos.; the temperature at the outset being 38°, but raised gradually to 82°.

For black upon a catechu-brown ground:—12 pieces of cloth: 1200 litres of water; 4.5 kilos. of garancin; 4.5 kilos. of lima wood; 2 kilos. of quercitron; 1.5 kilos. of sumach. Temperature, from 38° to 65°.

Red ground with black and brown pattern:—Cloth, 12 pieces: garancin, 9 kilos.; sapan wood, 6 kilos.; sumach, 3 kilos. Temperature, from 38° to 82°.

For puce-brown only:—Cloth, 12 pieces: garancin, 6 kilos.; lima wood, 20 kilos; quercitron, 4 kilos.; oak-bark, 4.5 kilos.; water, 1200 litres. Temperature, from 38° to 50°.

After leaving the dye-beck the goods are washed in the washing-machine. Without entering into the details of their construction, to give some idea of the vast capabilities of some of those machines we cite the following fact, mentioned by Messrs. Whittaker, of Manchester. Their machine will wash 6000 yards (= 3 miles and 720 yards) for all kinds of dyeing purposes, and 12,000 yards for all bleaching purposes, per hour, only requiring the attention of a person of 12 or 14 years of age. Several improved machines have been introduced by a great many makers, among whom are Messrs. Mather and Platt, Mr. Furnival, Mr. Barlow, Mr. D. Crawford, all which meet with very general approval. The washing in this instance is chiefly done with the view of getting rid of adhering vegetable matter.

As regards the dyeing with commercial alizarin (Pincoffs), this is performed precisely as is here described for garancin. Alizarin is used for dyeing upon cotton and calico in the same manner as garancin and flower of madder: its properties are very similar to those of flower of madder, but the colours are faster. Upon calico, double and triple purples, with black single and double roses and Turkey-red (see below), are obtained as easily with this product as with any preparation of garancin. The alizarin shades possess the great advantage of being acted upon by soap, acids, alkalies, and preparations of tin, without losing intensity, and at the same time they gain in brilliancy: it is therefore necessary to use one-eighth or one-tenth less of the mordant, to avoid obtaining deeper shades than would be produced by garancin or flower of madder. In dyeing with alizarin the colour should be moistened with warm water before being placed in the bath, otherwise it will float and perhaps stain the cloth. Since alizarin does not part with its colouring principle at a lower temperature than from 41° to 49° it is not necessary to pass the goods into the bath below 30° to 33°, but it is better to keep them at that heat two hours before proceeding to the boil: lime has a great affinity for alizarin, and

it is therefore necessary to attend to the purity of the water to be used, neutralising it, if required, with oxalic acid. Purpurin dyes with great facility and at a very moderate temperature; the bath is perfectly clear, and may serve until exhausted.

Upon calico, red and black mordants are dyed very quickly; a weak soap bath (clearing) of from 44° to 49° restores the whites and brightens the colours. Purple mordants take the colour with the same facility, but the shades are somewhat greyish. In order to fasten purpurin colours and preserve the whites it is necessary to mix purpurin with from fifteen to twenty times its weight of bran and a sufficient quantity of water at about 40°, and add it to a bath at about 55°, which is then heated so as to boil in about forty-five minutes, and kept boiling for the same time, during which the pieces are passed into it, and afterwards into a boiling bran bath; after which a simple washing will suffice to render the whites perfect.

To prepare a steam-colour with purpurin, for cloth mordanted with an aluminous mordant, the following is the best plan:—To the purpurin is added 20 per cent of its weight of carbonate of soda; the whole to be well ground together; hot rain-water is added, when a magnificent red solution is obtained, which is filtered and left to cool. It is then thickened with starch to the required consistence, and may be preserved without alteration for a long time. When required it is printed, steamed, and washed in cold water. With 20 grms. (about 300 grains) of purpurin per quart a good colour is obtained. If in filtering the purpurin solution there is any deposit on the filter, it may be used in ordinary dyeing.

We have now to direct our attention to the operation known as clearing (avivage): the colours obtained with garancin, alizarin (commercial), and purpurin are sufficiently pure and also quite brilliant enough not to require the operations necessary for madder-dyed stuffs for increasing or bringing out these properties. All that is required is a thorough washing, in order to restore to the whites the proper degree of purity. This purpose is attained by the application either of soap or of a bran bath, the latter chiefly applied to garancin browns (puce-colour), and to such patterns on white ground as do not contain purple. This branning is, strictly speaking, an avivage,* but one of a very mild character as compared with that in general use for madder-dyed materials.

For a puce ground, without any purple design, the following ingredients are used for 18 pieces of goods, at 100 metres each:—Water, 1200 litres; bran, 9 kilos.; cow-dung, 2.5 kilos. Temperature, 56°; duration of the bath, i.e., time of keeping goods in, 30 minutes.

For goods with white ground, without purple, again for 18 pieces:—Water 1200 litres; bran, 9 kilos.; cow-dung, 1.5 kilos. Temperature, from 38° to 57°; time, 30 minutes.

Branned goods are not afterwards soaped, but simply washed in the washing-machine for half an hour, with cold or tepid water. Soaping—that is to say, the immersion of the goods into a more or less concentrated soap solution, at a more or less high degree of heat, sometimes raised to the boiling-point of water—is performed, with garancin-dyed articles which contain purple, for the double purpose of better fixing that colour and for increasing its brightness.

^{*} Literally, a rendering more lively, and this signification is not precisely implied in the word clearing.

For goods containing much purple the soap solution consists of 8 kilos. of white soap and 1320 litres of water: temperature, 100°; duration of immersion, 1 minute. For goods with less purple the quantities are—Water, 1320 litres; white soap, 4 kilos.: temperature and time of immersion the same as above.*

These operations—viz., washing, branning, and soaping—are not sufficient to bleach very completely the unmordanted or the white portions of the fabric which have taken up, even in garancin-dyeing, some colouring matter, although far less so than is the case with crude madder. The goods are therefore subjected to the action of chlorine,—that is to say, run through a very weak solution of bleaching-powder. Garancin-dyed articles are chlored twice; the first operation, steam chloring, consists in passing the goods first through a very weak solution of bleaching-powder, and immediately after through a large tank filled with steam: the moist heat sets the chlorine (hypochlorous acid) free, and thereby causes the oxidation of the small quantity of colouring matter adhering to the white portions of the fabric.

It need hardly be said that the solution of bleaching-powder should be so dilute as not to injure the tissue, even very fine muslins and similar fabrics, and also not to deteriorate the colours. The second chloring is effected by making the goods, after having been moistened with the solution of bleaching-powder, pass over a series of partly hollow cylinders, heated by means of steam, whereby, during the drying, the bleaching also is completed. We give below some receipts as employed for these purposes, but in this country the aqueous solution of chlorine is not very commonly used, owing to the fact that it is a less certain agent, unless prepared with great care and used within a very brief time after it has been prepared.

For goods containing much purple the solution for the first chloring consists of—50 litres of water; 2 litres of chlorine water; 16 grms. of ultramarine: the latter substance performs here the same functions as the various kinds of blues used in the laundries. The second chloring solution consists of—Water, 16 litres; chlorine water, 2 litres; ultramarine, 2'240 kilos.

For puce-brown coloured ground with a white pattern the first chloring is made up of—12 litres of water; 2 litres of chlorine water; 15 grms. of ultramarine. Second chloring solution:—Water, 16 litres; chlorine water, 2 litres; ultramarine, 1.120 kilos.

For grey dyed goods, first chloring liquid:—Water, 24 litres; chlorine water, 2 litres; ultramarine, 15 grms. Second solution:—Water, 120 litres; chlorine water, 2 litres; ultramarine, 1 120 kilos.

For goods with much red, first solution :- Water, 40 litres; chlorine water,

* The soap for clearing madder purples is generally selected less alkaline than that used for reds and pinks. For the former a good composition is-

	Fatty acid					 60'40
	Soda					 5.60
	Water				• •	 34'00
For reds and pinks t	he following i	s prefe	rable	*****		100.00
Tot tens and burg t	-					
	Fatty acid		0.0	* *		 59.53
	Soda		* #			 6.22
	Water				100	 34.00
						100:00

2 litres; ultramarine, 15 grms. Second solution:—Water, 40 litres; chlorine water, 2 litres; ultramarine, 1°120 kilos.

For goods dyed when much catechu has been added to the garancin, the first chloring solution consists of—Water, 24 litres; chlorine water, 2 litres; ultramarine, 15 grms. Second solution:—Water, 60 litres; chlorine water, 2 litres; ultramarine, 1.120 kilos.

Goods dyed with the same colours, but with white ground, are treated in the same manner, but the ultramarine is dispensed with. It is quite evident that the chlorine water used should be pure, and quite free from hydrochloric acid.

Fig. 22 gives an idea of the arrangement of the rollers or cylinders above alluded to.

When chloride of lime or bleaching-powder is used it is applied in several ways: madder-dyed goods for clearing are run through a very dilute hot solution of the bleaching-powder, until the dyer or clearer considers the whites sufficiently restored and bright. For garancin-dyed fabrics the same process may be adopted, but experience has shown that the higher temperature employed in garancin-dyeing tinges the whites more deeply than madder, while the less stability of the colours produced renders it dangerous to let the pieces run long enough to clear the whites. In consequence, two other methods of clearing garancins are adopted:-The first consists in padding the piece to be cleared in solution of bleaching-powder, at a specific gravity of from 1.075 to 1.010: the padding is done by an engraved roller, and so arranged that only a small quantity of the bleaching-liquor is transferred to the piece, which is next passed over the steam-chest or drum, and either washed off or finished without washing. The other and better method consists in padding the pieces in bleaching-powder solution not quite so strong as the last, and then passing them through a steam box, in which they remain two or three minutes exposed to low pressure steam, and from this pass through three or four boxes of water to wash them. The only delicate point in clearing is to hit such a strength of the clearing liquor as shall effectually clear the whites without acting too much upon the coloured portion. In light shades this is not an easy matter, and it is therefore preferable to clear them in the beck, where they can be watched.

The application of chlorine instead of grass bleaching for garancin-dyed goods was first introduced into France in the year 1847 by Messrs. Blech, Steinbach, and Mantz. A very great saving of time and money is the result, along with a far better finish of the goods. A fact which could not have been foreseen, viz., that the dyed portions of the cloth are less readily and plentifully moistened by water than the white portions, contributes largely to the proper action of the chlorine, which consequently has more effect upon the white than upon the coloured parts of the tissue. After the chloring the goods are ready for being starched and blued, and calendered, as the case may require, and finished for packing. When madder-dyed goods leave the beck the white portions of the fabric are very much soiled, the colours are flat, without life or brilliancy, and are not quite so fast as is desirable. The operations by means of which the beautiful results with which the public is familiar are obtained are of a complex nature, and vary for different styles. The reds, lilacs, and purples do not stand equally well the action of the same

chemical agents—what beautifies the one injuring the other; so that if both these colours occur on the same piece the beauty and brilliancy of one of them will be of necessity sacrificed to the other.

Even as late as the middle of the first quarter of this century field bleaching and boiling the goods in bran-water were the chief modes of clearing in use. The application of soap for clearing purposes dates from the year 1804, when it was first used by M. D. Kæchlin, who also appears to have occasionally employed chlorine.

The modern processes for clearing madder-dyed goods have been gradually developed, and are more the result of accidental discoveries than of a regularly studied course of research. For clearing of rose-reds and reds by themselves almost every printer and dyer has his own peculiar method, but generally the following is an outline of the process applied: - Soap baths, a tin-salt bath, and a boiling up of the goods under pressure with crystallised carbonate of soda and soap. The ingredients used and their proportions may be learnt from the undermentioned examples:-I. Soap bath-Water, 1200 litres; white soap, 4 kilos, for 900 metres (984.267 yards) of cloth; temperature, 56°; time of immersion, one hour and a quarter. 2. Washing in machine with cold water. 3. Bath of nitro-muriate of tin (perchloride of tin)-Water, 800 litres; solution of the tin preparation, 1.5 litres for 300 metres of cloth; temperature from 56° to 62°; time of immersion, from fifteen to twenty minutes. 4. Washing in machine as in No. 2. 5. Second soap bath-Water, 1200 litres; soap, 3 kilos.; cloth, 900 metres; temperature, 94°; time, three quarters of an hour. 6. Again washing in cold water. 7. Third soap bath-Water, 1200 litres; soap, 3 kilos.; cloth, 900 metres; temperature, 94°; time, three quarters of an hour. 8. Another washing in cold water. 9. Boiling in a closed boiler under pressure—Water, 1200 litres; soda crystals, 2'5 kilos.; soap, 2'5 kilos.; time, two hours. 10. Again washing in cold water. 11. Warm bath at 50° during thirty minutes' time.

Field bleaching in combination with some of the above operations is still in use for certain styles, chintzes, and furniture prints, because the tints become more transparent. As regards the action of these different operations, at the first soaping the goods lose much colouring matter; the liquid, indeed, becomes rather deeply red. This is partly due to the colouring matter, which had been temporarily fixed to the white portions of the tissue, and partly also to such of the constituents of the madder as yield less fixed permanent colours than alizarin, viz., purpurin, and, more so, pseudopurpurin combined with the mordant while in the beck.

Dr. Schützenberger has demonstrated that properly mordanted cloth dyed by means of pseudopurpurin yields to a soap bath the greatest portion of its colour. Soap, moreover, has the effect of dissolving the greater part of the yellow matters, which cause the dulness of the colours. The action of the soap is not simply detergent, for in consequence of a more or less complete decomposition of the soap,* a portion of the fatty acid is precipitated on the tissue, and combines either chemically or mechanically by a strong adhesion with the coloured lake, thereby communicating to that substance a far greater fastness and power of resisting the action of light and solvents than it

^{*} The reader is reminded that soap is in a chemical sense a salt made up of a base and a fatty acid.

previously possessed. That this effect is really caused by the soap is proved by the fact, that if the dyed fabrics, on being taken from the dye-beck, after a wincing in cold water for the removal of adhering particles of dye-stuff, were immediately placed in a bath of nitro-muriate of tin, the colours would be far more attacked than is the case in the ordinary process of clearing. By the treatment with the tin preparation, instead of which very dilute nitric acid may be used, a remarkable effect is produced. While undergoing this treatment the reds and pinks seem almost destroyed, becoming orange, but by the subsequent soap bath the fine shades are brought out very vividly, exhibiting also a peculiar "bloom," which before the application of the tin-salt bath was not seen at all. The intensity of the colour is, however, slightly diminished, but this effect is taken into consideration during the dyeing process, care being taken to procure rather too deep a colour.

The experiments of Schlumberger have proved that the acid of the tin bath takes away a small portion of the alumina, while also some of the oxide of tin becomes fixed, the acid, moreover, removing the last portions of yellow matter. M. Persoz has thought that the tin bath might perhaps have a peculiar effect upon the principal colouring matter by entirely altering it, but this view is certainly not well founded, since more recent experience has proved that pure alizarin may be extracted from dyed fabrics which have been submitted to the clearing operations. It is far more likely that the effect of the nitro-muriate of tin is the complete elimination of the purpurin, pseudopurpurin, and the yellow colouring matters. The two former substances yield with aluminous mordants a red, less bloomy, bright, and vivid tint than is produced by alizarin, and therefore the peculiar effects of the tin bath are readily accounted for. To this should be added, that the fixing of some oxide of tin instead of the eliminated portion of alumina plays an important part. The second soap bath also, at nearly boiling heat, does not simply act as detergent, but it is probable that again some of the fatty acid is fixed. As regards the action of the last boiling under pressure, it is very difficult to explain precisely what it effects. According to M. Persoz, the effect is the fixing of a larger quantity of fatty matter, and there is good reason to adopt this as a correct view. It is supported by the following facts:-Red madder-dyed cloth, which has either not been cleared at all or only incompletely so, turns, on being treated with acids, an orange-red, and, on being next immersed in milk of lime, becomes bluish; but after a complete process of clearing, and especially after the boiling under pressure, as described, the cloth stands the action of these agents without thereby undergoing any perceptible change; the effect, therefore, produced by the said boiling is somewhat analogous to the well-known properties of the so-called Turkey-red, which, as we shall presently see, owes its great power of resistance to the presence of a modified fatty substance in combination with the aluminous lake. The clearing of the purples, puce browns, and blacks, where no red is present on the cloth, requires, for bringing out all the beauty of these colours in the highest degree of perfection, the agency of chlorine or of bleachingpowder. Without doubt the main action of the hypochlorites of lime, of soda, and magnesia, as industrially applied, is oxidising. It is very probable that the iron mordants undergo in the dye-beck a partial reduction, and that the proper degree of oxidation required is restored by the application of the hypochlorites. On the other hand, the colouring matter itself is certainly not acted upon in this way, since it is possible to extract pure alizarin from cloths dyed purple, lilac, and brown, and cleared. When pincoffin is used as a dye material the purples produced require no clearing at all, and the explanation may be, that either the stronger heat applied has had the effect of destroying the foreign matters which, while becoming fixed to the mordant, affect the purity of the colours, or this overheating neutralises the reducing effect of the organic substances, and as a consequence the peroxide of iron of the mordant does not undergo a partial reduction, and therefore the application of chlorine is needless. Instead of the nitro-muriate of tin, which would injuriously affect the purples, browns, and blacks, sulphuric or oxalic acid is applied, but their use should be avoided wherever possible, since even without these the clearing process affects the browns and blacks.

For purples, lilacs, browns, and blacks alone the ingredients and quantities are as follows:-Cloth, goo metres; water, 800 litres; solution of chloride of lime (sp. gr. 1.060); temperature, from 50° to 100°; time, quarter of an hour. Washing in machine with cold water and next the first soap bath:-For 900 metres of cloth-Water, 1200 litres; soap, 4.5 kilos.; temperature, 88°; after the first half hour another 1.5 kilos, of soap are added, and the operation continued for a further quarter of an hour. Again a washing in the machine, followed by second chlorine bath of the same composition as the first, but the temperature from 50° to 63°; time, twenty minutes. Again a washing in the machine with cold water. Second soaping, for 900 metres of cloth:-1200 litres of water and 2 kilos. of soap; temperature, 94°; time, twenty minutes. Again a washing, followed by a bath of bleaching potassa liquor* composed of-Water, 1200 litres; carbonate of soda, 4 kilos.; potassa bleaching liquor, 10 litres; for 900 metres of cloth at a temperature of 56°, and to last for twenty minutes; this treatment is followed by washing in cold water in the machine and next drying. No acids are employed, the operations being performed with the aid of soap and the hypochlorite.

When red, brown, and black are printed on the same cloth the clearing operations are conducted as follows:-First, a bleaching bath composed of 800 litres of water and 4 litres of bleaching-powder solution at 1.060 sp. gr. for 300 metres of cloth; temperature, from 31° to 44°; time, fifteen minutes. Second, washing in the machine, followed by the first soap bath, composed, for goo metres of cloth, of-Water, 1200 litres; soap, 4 kilos.; temperature, from 44° to 56°; time, three quarters of an hour. Again a washing in cold water, and next, if the black is still deep enough coloured, a bath of nitro-muriate of tin, but if the black will not stand this a bleaching bath is applied made up, for 300 metres of goods, of 800 litres of water and 4 litres of bleaching-powder solution at 1.060 sp. gr.; temperature, 44°; time, twenty minutes. After this again a washing in cold water, and next the second soap bath, consisting of-Water, 1200 litres; soap, 3 kilos., for 900 metres of cloth, to be kept at a temperature of 94° for fully three quarters of an hour. Another washing in cold water is followed up by a third soap bath made up of-Water, 1200 litres; soap, 2.5 kilos., for goo metres of cloth; temperature, 94°; time, again three quarters of an hour. Again washing in cold water, followed by the third bleaching-powder bath,

^{*} A liquid somewhat akin to the well-known Eau de Javelle (hypochlorite of soda), but containing potassa instead. Magnesia will be found preferable.

consisting, for 300 metres of cloth, of 800 litres of water, 1.25 kilos. of soda crystals, and 5 litres of bleaching-powder solution at 1.060 sp. gr.; temperature, 50°; time, thirty minutes. Again a washing in cold water, and, lastly, drying ends these operations.

When purples, lilacs, red, and black are printed on the same piece the clearing operations and ingredients used are the same as just described, but instead of the bleaching-powder bath use is made of a bath made up of—Water, 1200 litres; crystals of soda, 4 kilos.; potassa bleaching liquor (hypochlorite), 10 litres, at a sp. gr. of 1°044; cloth, 900 metres; temperature, 38° to 44°; time, twenty minutes; washing and drying. The dry goods are calendered,* next starched and blued, dried, and a second time calendered. Purple grounds and white designs require a larger quantity of ultramarine blue.

We have now to consider a totally different application of the colouring principles contained in madder, which may be explained in a few words, first, as follows:-Instead of printing on the mordant and immersing the prepared cloth bodily into a dye-beck containing the madder, the colouring matter itself is printed on to the cloth, after having been brought into a suitable state of solution. In this instance we meet with three distinct modes of application; either the cloth itself is first thoroughly mordanted all over with acetate of alumina or any other required mordant; or the colouring matter and the mordant are so prepared as to form together the elements of the lake to be fixed to the cloth; or, lastly, the lake previously and separately prepared, and in an insoluble state, is fixed by means of a plastic mordant, as, for instance, albumen. The first experimental trials in this direction were made in the year 1827 by Messrs. Robiquet, Colin, Lagier, and Persoz; but not before ten more years had elapsed did M. Gastard, at Colmar, succeed in printing on the large scale the colouring matters of madder upon previously mordanted cloth. It need hardly be observed that in this mode of proceeding there can be no question whatever about the use of madder or any of its preparations. such as garancin, for instance, since all of these contain the ligneous inert fibre, and therefore the concentrated extracts of madder can only be applied in this instance. M. Gastard has proposed two methods of operation for this purpose—(1) the thorough mixing of colorin (a very rich alcoholic extract of madder, formerly made by Messrs. Lagier and Thomas at Avignon) with gum or starch paste and acetate of alumina, and steaming after it has been printed on the cloth; (2) the cloth is mordanted all over with acetate of alumina (preceded sometimes by an oiling operation, about which further details will be given under the head of Turkey-red), the mordant is fixed as usual, the thickened colorin is printed on the fabric, which is next steamed, and afterwards cleared as for reds and rose-pinks. This operation may be also performed with iron mordants as for brown; in that case the ground colour of the cloth will be coloured by the mordant itself, but this buff may be removed by passing the cloth through a tepid solution of bitartrate of potassa. The rather high price of the colorin has been the great obstacle in the industrial execution of this process on the large scale. In the year 1838 M. Fauquet

^{*} That is to say, undergo an operation which, in effect, is the same as the ironing of linen made up for use as clothing, but which in this instance consists in passing the goods between two well-polished and bright cylinders made of copper or steel and heated by steam internally.

obtained a brevet d'invention* for an application of an improved extract of madder, and Messrs. Girardin and Grelley made successful experiments on the application of their ammoniacal solution of colorin thickened with gum. After steaming the cloth so treated had only to be washed in cold water. This process had the additional advantage of being applicable to fabrics the grounds of which had been dyed black by means of logwood, or brown by means of catechu, both of which colours do not stand the clearing process. None of these trials and experiments ever came really into general practice, and only as late as the year 1855 was introduced what is known as M. Hartmann's method, which has been used to a limited extent by the firm of Schwartz-Huguenin at Mulhouse, although this method has been entirely superseded by another invention due to M. Pernod.

We record here the manner of its execution according to the statements of M. Al. Rack. The cloth is mordanted with acetate of alumina, first, by being passed through a solution of that salt at 1.022 sp. gr.; next dried, aged at ordinary atmospheric temperature for twelve hours, cleansed by means of silicate of soda, and further proper treatment, and next dried, after which comes a second mordanting in a bath of acetate of alumina at 1.036 sp. gr., followed by the same cleansing and other operations. The colouring matter (an alcoholic extract of madder) used to be incorporated with soap solution, but since the so-called green alizarin was discovered, this latter substance in the state of undried paste, and containing from 60 to 70 per cent of water, has been sub-

stituted for this extract.

The dried green alizarin can also be employed for this purpose, after having been previously mixed (in the proportion of 65 parts of soda solution and 35 of alizarin) with a solution of caustic soda at 1.007 sp. gr. When the undried pasty green alizarin is used there are added to I litre of this material 250 grms. of gum, previously reduced to powder. This mixture keeps well. For the purpose of colour printing the following mixture is employed:- I litre of thickened alizarin; 0.4 litre of warm soap lye, prepared with 100 grms. of soap to the litre; I litre of gum water. This mixture has to be applied at once, because it is liable to be spoiled by the coagulation of the soap. Sometimes, also, this mixture is diluted by taking I kilo. thereof, and mixing this with I kilo, of a thickening fluid consisting of 4 litres of gum water and I litre of hot soap solution containing 100 grms. of soap; or, again, I kilo. of the alizarin mixture with 1250 grms. of the thickener. After the printing and drying the cloth is steamed for two hours, next washed with clean cold water, in a running stream if possible, and next scaped at a temperature of 20°. If required a cold and weak bleaching-powder bath may be applied.

The purpurin and yellow alizarin discovered by M. Kopp may be employed for colour printing purposes by being first dissolved in weak caustic soda solution, next thickened and printed on to properly mordanted fabrics, and,

lastly, steamed.

As regards the printing of madder lakes and the fixing thereof on cloth

^{* &}quot;Technologie de la Garance," par M. Girardin (at present Doyen de la Faculté des Sciences at Lille), Paris, 1844.

[†] This amounts to a quantity of less than I per cent of dry caustic soda, since, according to the tables collocated by Dr. Gerlach (see "Chemical News," vol. xxi., p. 155), the sp. gr. of an aqueous solution of that alkali at 15° equal to 1'012 holds exactly 1 per cent of the dry substance.

by means of animal mordants, such as albumen, this has never been a successful operation, for the very good reason that the madder lakes, even the best prepared, when thus employed, do not exhibit the same transparency and pleasing effect as the dyed colours produced by madder; it is, moreover, very difficult to prepare deep red madder lakes, while hitherto neither purple nor brown madder lakes have ever been made with anything like a satisfactory result even to serve as pigments.

We cannot enter fully into the details of the so-called discharge and resist processes destined to produce white patterns on a coloured ground; but although this subject is in reality a speciality of technology, and therefore requiring a separate treatise, it is hoped that the following particulars will give the reader some idea of these operations. By the word discharge (enlevage in French) is designated any compound or mixture which has the property of bleaching, or taking away, the colour already communicated to a fabric. Their use as regards madder-dyed goods is chiefly confined to the Turkey-red dyed fabrics, but is applicable if required upon lilac and other madder shades. The process generally known as Monteith's consists in the direct application of a solution of chlorine to the dyed fabrics. The Turkey-red dyed fabrics are placed in folds properly smoothed and arranged between two thick cast lead plates, both of which are perforated with the design to be produced, the perforations exactly corresponding; the cloth is then pressed between these plates with considerable force, and the plates secured. By this mechanical contrivance the wetting of the portions of the cloth tightly pressed between the unperforated parts of the plates is very effectually prevented, while any liquid poured on the upper plate will gradually filter through the cloth from the perforation of one plate to the corresponding on the other. The passage of the discharging fluid (bleaching-powder with an excess of free acid) is assisted by currents of air. When the colour is discharged clear water is passed through, and the pieces then washed and finished. As might be expected from the nature of the process, the edges of the design are not sharp and clear, because, notwithstanding any practical amount of pressure, capillary attraction will assert itself, and consequently the edges of the designs are blurred.

The other process frequently used for this purpose is the discovery of M. D. Keechlin and Mr. Thompson. It consists in printing a highly acid colour upon the cloth to be discharged, and then plunging it into a solution of bleaching-powder in water; the acid acts upon the bleaching-powder, causing a disengagement of chlorine, which destroys the colour upon the spot where the acid is printed. It will be readily understood that the difficulty in this process consists in confining the discharge to the points printed on, for it is not possible to hit the quantity of chlorine just necessary to discharge the colour, and any excess generated spends itself upon the colour in the neighbourhood, unless some precautions are taken. By having a considerable excess of lime (chalk may be added with some advantage) in the bleachingpowder, and by not leaving the goods in any longer than is absolutely required, and also by care being taken that the cloth is properly dried before being immersed in the bleaching solution, very regular results can be obtained. Besides producing a white design, there are discharges which, whilst destroying the red colour, leave another in its place, or the basis for producing another. As examples of the composition of some of these discharges, we

quote the following:—White discharges on Turkey-red—I gallon of water; rolbs. of tartaric acid; 7½ lbs. of pipeclay or china-clay; I pint of gum water;—I½ lbs. of bichloride of tin; I gallon of hot water; 9 lbs. of tartaric acid; Io lbs. of pipeclay; 3 quarts of gum senegal water. These can only be properly applied by blocking, but the following discharge for machine work may do for light designs:—I gallon of water; 6 lbs. of tartaric acid; I½ lbs. of starch. As an instance of discharge for red and the reproduction of blue on the discharged spot, we mention the following mixture:—2 gallons of muriate of tin; I gallon of prussian blue pulp;* I gallon of water; 5 lbs. of tartaric acid, to which, after having been dissolved and mixed together, are added 2 gallons of thick tragacanth gum water. The excess of acid discharges off the red, while the blue part not being acted upon, remains.

A resist (French, réserve) in calico printing signifies any suitable composition applied to the portions of the fabric in order to prevent the decomposition of the colour or mordant upon those portions of the cloth. The parts thus protected may be either the original white fibre of the cloth, or it may be some coloured part which is required to be preserved unaltered, while the remainder is covered with some coloured design. Resist compositions intended for this latter purpose are usually called pastes, and the colour so preserved is said to be pasted; resists may, moreover, be either chemical or mechanical, or both combined, according to the nature of the colour or mordant to be resisted and the manner in which it has to be applied. The best and only safe resist for iron and red liquor mordants is lime-juice, chiefly citric acid. If of fair quality and of proper strength it leaves nothing to be desired. Good limejuice at 15° Tw., thickened with calcined farina, will resist all the iron and alumina mordants in use for madder work, and at 30° Tw. it is strong enough as a resist for garancin styles. Oxalic and tartaric acids and bisulphate of potassa will act as resists, but are inferior to lime-juice or citric acid. Citrate of soda or potassa also form a good neutral resist, and are usually employed along with pipeclay.

The reserves or protecting resists are commonly applied by the block, and act chiefly mechanically, as may be inferred from the undermentioned resist paste for chintz, made up of—Water, 6 gallons; neutral arseniate of potassa, 15 lbs.; pipeclay, 40 lbs.; calcined farina, 30 lbs. The arseniate of potassa has some resisting power, but its use in combination with pipeclay is owing to its drying up in a dense, somewhat gummy mass, which gives solidity to the pipeclay, and makes it more capable of withstanding the effects of friction. Another neutral paste is made from citrate of soda mixed with pipeclay and calcined farina.

A most ingenious means of obtaining reserves on fabrics is the invention of Messrs. Onfroy and Co., of Paris: this process is the more advantageous, because the chemical reserves in general use are imperfect in composition, of difficult application, and still more difficult to remove. The process in question consists in punching out patterns from a sheet of cardboard lined with guttapercha in such places as are intended to remain white or reserved. The cardboard is then rolled on the pressing cylinder of the printing machine, so that

^{*} Under this name are known to printers and dyers a variety of mixtures made up of yellow prussiate of potassa (ferrocyanide of potassium), protochloride of tin, or bichloride and water.

when the machine is working the parts of the pattern which have been cut out receive the impression, and thus form the reserve parts of the pattern. It is evident that to obtain satisfactory results the greatest precision must be observed in applying the cardboard to the pressing cylinder, so that the engraving roller will only press where required. The great advantage of this mode of producing reserves is that, by employing a pressing roller of sufficient diameter, reserves of large surface can be easily obtained. Under the name of conversion is designated a certain modification of the shade of any colour produced on cloth by means of the intervention of some chemical agent. This modification may be total or only partial, that is to say, brought on over the entire coloured surface, or only in certain portions thereof, as limited by the engraving roller. In order to illustrate this process the following particulars may serve: - I. Some stripes or any other design is printed on in acetate of alumina prepared for rose-red and mixed with nitrate of alumina. If after drying there is next printed on a finer design with acetate of soda, this substance wherever it comes into contact with the mordant first applied will cause double decomposition to take place between the nitrate of alumina and the last-named salt, and the result of this decomposition will be to give increased strength to those portions of the mordant where such contact with the acetate took place. Consequently the effect after dyeing will be the production of a double rose-red. Similar effects can be obtained with the iron mordants, and in that way double purples are produced. 2. Intersecting stripes of purple or red will at the points of intersection have a deeper colour by a similar application suitably executed. 3. Rose-red and purple may be modified by the addition of catechu to the mordants, and afterwards a design in bichromate of potassa may be printed on. Wherever this latter material comes in contact with the previously applied mordants the oxidation of the catechu will cause it to develop its peculiar brown colour, but over the rest of the pattern it will disappear by means of washing immediately after the application of the bichromate, so that on leaving the dye-beck the madder colours will have only become developed just as if the catechu had not been added to the mordant. 4. A mordant for good red is printed on, dyed, and cleared, and next upon some portions of the same fabric a solution of oxalic acid is printed on, the cloth is next steamed, and by this means the action of the oxalic acid is brought into full force, and wherever it has been applied the red colour is converted into rose-red. 5. By crossing stripes of a red madder-dyed and cleared pattern by means of iron buff stripes, we shall have three different shades of colour, viz.—A, red not acted upon; B, buff upon a white ground; and C, the shade of colour due to the superposition of red and buff. If there be next applied to this a pattern or impression of oxalic acid, and the fabric afterwards steamed, the effect will be as follows:-The buff will have been destroyed upon the white as far as the acid came into contact therewith; where the red, the buff, and acid meet violet will appear, from which it may be inferred that the acid dissolves the alumina in preference to the iron, and consequently gives rise to the formation of a lake having that oxide as base. 6. Fine red stripes are first dyed by means of madder to which nut-galls have been added, the tannin thereof fixed to the mordant and which has resisted the clearing operations is invisible, the only effect being that it slightly alters the peculiar beauty of the red; but if after the clearing there are printed on this cloth stripes of buff (an iron mordant), a black will appear on those stripes which are touched by the buff, while that colour is not altered on the white portions. This proves that during the dyeing process the tannin has only become fixed on those portions of the cloth which are mordanted with alumina. A similar effect may be obtained by substituting for nut-galls any other astringent, as, for instance, quercitron or sumach. 7. Cloth uniformly dyed with Turkey-red is in some parts covered with a thin paste containing tartaric acid and an iron salt. After drying the cloth so prepared is immersed in a bath containing a solution of bleachingpowder. This substance does not act upon the Turkey-red dyed portion at all, but the portions where the acid is printed are discharged, while at the same time on these spots the iron is deposited, hydrated oxide being precipitated on the fibre. If the cloth is next, after previous washing, placed in a somewhat acidulated solution of ferrocyanide of potassium, prussian blue is produced upon the portions of the cloth where the red was discharged. 8. M. Carlos Keechlin has published* the following interesting effect of conversion operated upon a madder-dyed cloth:-

M. Persoz first observed that madder purple when treated with hydrochloric acid is turned to an orange-yellow: if cloth so treated is next placed in a milk of lime bath it becomes a beautiful bluish-purple, exhibiting great brilliancy. When garancin-dyed purples are similarly treated there is only an amaranth colour produced. This difference as regards the garancin is simply due to the absence of lime from the purple-lake which garancin yields on cloth; for if there is added to the beck containing the garancin an excess of lime, so as to produce a colour which resists strong soaping, the treatment with acid, and subsequently with milk of lime, will have the same effect as on madder.

When a pattern dyed purple with madder or fleur de garance is immersed in sulphuric acid, sp. gr. 1°116, and next washed in water, and afterwards immersed in a solution of aluminate of soda without excess of alkali (the aluminate made from Bauxite), the pattern will become instantaneously red, and the quantity of alumina which becomes fixed is in the direct proportion to the strength of the iron mordant originally printed on the cloth, and having served to produce the purple pattern. It therefore appears that the acid (sulphuric just named) discharges the iron of the mordant, leaving the colour untouched, and the latter—as soon as brought in contact with the aluminate of soda—attracts alumina therefrom, combining with it instead of with the iron which had been taken from it. The reds so obtained may be soaped, but do not resist this operation so well as do the reds obtained by ordinary methods.

As regards the opinion of M. C. Kæchlin upon the action of the lime for fixing the purples, M. Mathieu-Plessy observes that the alcoholic extracts of fleur de garance and garancin, neither of which contain any lime, yield in dyeing—distilled water being used—very fast purples, which, if treated as above described with hydrochloric acid, behave exactly as madder-dyed purples. This fact proves that, as regards the cause of the want of fastness of garancindyed purples, there is some unknown circumstance, and that it is not solely due to the absence of lime.

^{* &}quot;Note sur la Teinture par Substitution" (Bulletin de la Société Industrielle de Mulhouse, vol. xxviii., p. 119).

We have now to consider the Turkey-red, as it is usually called, because, as we shall presently see, this mode of madder-dyeing was introduced into Europe from the East. Turkey-red is highly important, as much for the various substances which concur in producing it as for its peculiar beauty, intensity, and permanency. As far as the history of this branch of dyeing is concerned we briefly note the following:—Undoubtedly this peculiar mode of applying madder to cloth is of Indian origin, where, according to the account of M. Le Goux de Flain, the cloth intended to be dyed is first steeped and padded about in buffalo's or sheep's milk, and next exposed to the sun. From India the art of preparing the cloth as required for this dye came over to the Levant, and was introduced into France in the eighteenth century by some Greeks.

Before entering into the full details of Turkey-red dyeing, and discussing the various points specifically, it will be advisable to give a concise preliminary sketch as follows: - This process consists in the application of the four undermentioned operations: (a), mordanting of the tissues with oil; (b), the application of tannin (alum); (c), the dyeing in madder, or also in garancin; (d), the clearing and brightening. The first operation is performed on the goods, which have been previously well bleached and bottomed, by liming and bowking: they are immersed in a mixture of a peculiarly sour olive-oil (huile tournante), pearl-ash, sheep's dung, and water. On being removed from this mixture they are slightly rinsed in water, and next brought over into a fresh mixture of the oil, pearl-ash, and water. After being well worked about in this liquid they are exposed to air, spread out on grass-plots, and placed as if for the purpose of bleaching if the weather be warm, but in winter stove-heated rooms are resorted to. This operation of oiling is repeated, in some instances even seven or eight times. The excess of oil, or that at least which has not changed its character by oxidation and alkali, is removed by steeping and washing. The next process is the galling, as it is technically termed, and this is sometimes done separately, at other times also combined with the application of alum, but so that the immersion of the pieces in decoctions of materials containing tannin is effected first, and followed by the steeping of the goods in an aluminous mordant. The materials employed as astringents are nut-galls and sumach, which are applied as infusion decoctions, with which the pieces are padded. After having been dried, the goods are padded in a solution of alum previously neutralised with carbonate of soda; dried and alumed a second time, and next aged for some days; they are then fixed, by passing in warm water containing ground chalk. When washed out of this the goods are ready for dyeing in madder or garancin. On leaving the dyebeck the goods, which are of a very heavy brownish-red, are brightened by two or three soapings, or a passage through acid.

Resuming briefly this important subject, we may state that the bleached tissues, or yarn (animal fibres, however, wool and silk, are never so treated) are first soaked in what is commonly, in this country, called Gallipoli* oil, of a peculiar quality, because the oil to be suitable for this use must, when mixed with a small quantity of an alkaline carbonate, form a white emulsion, and this is due—as we know from M. Pelouze's researches—to a ferment which the oil, when liberated from the berry, carries with it, and which resolves it

^{*} Gallipoli is the name of an Italian sca-port town, whence olive oil is largely exported: the oil here alluded to is, however, an inferior kind, at least as far as its consumption for food is concerned.

into its component parts, viz., glycerin and fatty acids. The oil so modified is adapted for Turkey-red dyeing. The textile fabrics saturated with these acids are dipped in a solution of carbonate of soda,* and then exposed to the action of the air, or air and steam, in a warm room: after this treatment has been repeated a sufficient number of times the goods are passed through a solution of nut-galls, then into a solution of a salt of alumina, and next through warm chalk water. They are next washed, dyed by being boiled for two or three hours in a bath to which madder-root or garancin has been added; lastly, the brilliancy of the colour is brought up by boiling in a strong soap solution. Up to this day no thoroughly satisfactory explanation of the real effect of the application of the oil in this process has been given, and since it is an acknowledged fact that no Turkey-red can be obtained without this application, we do not enter into any speculative discussions on this subject, but simply give a detailed account of the operations just indicated, with the observation that the processes are varied by different manufacturers according to their own experience. The goods, first properly bleached, are padded in an emulsion made of the oil † and of an alkaline carbonate: the olive-oil applied for this purpose has the characteristic property of readily yielding a permanent emulsion when shaken up with an alkali. The mode of testing the oils for this purpose consists in beating up I part of oil with from 36 to 40 parts of soda-lye containing about 1 per cent of dry caustic soda. If, after standing for some five or six hours, the mixture is found to be homogeneous, without any sign of a separation of the oil, it is admitted as of fit quality. This Gallipoli oil is prepared from rather unripe olives, which are steeped for some time in boiling water before being pressed. This treatment causes the oil to contain a large proportion of extractive matter.

In France the best and ripest olives yield, as is well known, a small quantity of oil spontaneously without pressure; gentle pressure is next applied, and lastly the pressed cake is placed in boiling water for a couple of hours, and on being then pressed again, yields what is locally known as huile d'enfer used for soap-making, and burning in lamps, and is very suitable for the purpose

of mordanting Turkey-reds.

According to M. Persoz any oil may be rendered easily emulsive (tournante) by beating up therewith two yolks of egg per litre. This statement does not hold good for the drying oils, since this was purposely tried several years ago by the elder M. Prévinaire, at Ghent, who found that neither linseed, hemp-seed, nor poppy-oil would answer the purpose, not even when previously beaten up with yolk of eggs. This is confirmed by Professor Mulder's extensive researches on drying oils, which, according to him, belong rather to the class of substances producing caoutchout than to the true fatty oils. According to the experiments made by M. E. Schwartz the action of the alkalies, preferably carbonates, or even bicarbonates, is not simply to form an emulsion, but also to predispose the oil for the peculiar changes it has to undergo afterwards. It is considered by many manufacturers necessary to add sheep- or cow-dung

^{*} The reader will no doubt be struck with discrepancies in the details of the process as here laid down, but there is scarcely any dyeing operation in which so many variations occur, all, however, tending to one general result.

[†] In Europe generally an inferior kind of olive-oil is used, but in the East (India, Persia), where the natives still produce the finest and fastest reds, many kinds of oil are used—for instance, fish-oil, lard, and other fatty matters—very successfully.

to the mixture of oil and alkali, it being thought that these materials animalise the cloth; but it is more probable that since these materials contain principles of bile in a high state of activity they exercise some influence tending to a peculiar decomposition of the oil, while, moreover, the albuminous compounds present aid the formation of the emulsion. Be this as it may. the cloth-after having been uniformly worked about and padded in the mixture, as described-is dried in a stove-warmed room, and next placed on the grass, or, if the weather be hot and fine, the cloth is at once dried in the sun. The joint action of a suitable temperature with air, light, moisture, and the alkaline carbonates, brings about a transformation of the oil in a peculiar manner, the true nature of which is unknown to us. Instead therefore of entering into hypothetical discussions on this subject, we prefer to lay before our readers the results of the experimental researches made by some chemists, among whom is M. Weissgerber, assistant to the late M. Persoz. He took oiled and cleansed cloth, and exhausted it by means of aceton. After repeatedly applying this fluid to the cloth, he observed that it lost more and more the property of attracting the colouring matter of madder from the dye-beck. On evaporating the acetonic solution in the water-bath he obtained a viscous liquid residue, which was found to consist of two substances, -one a solid body, the other a liquid. This latter did not, on being saponified, yield even the slightest trace of glycerin, and when the original liquid was applied to cloth it dyed up beautifully in the beck with madder.

Dr. Schützenberger has recorded the following experiments:-He took cloth dyed and cleared for Turkey-red, and treated it at a gentle heat with very strong alcohol acidified with sulphuric acid. The liquid thus obtained was saturated with ammonia, the alum precipitate separated by filtration, the solution next concentrated by evaporation and precipitated by the addition of water. The substances thus thrown down were removed by filtration, and, after washing and drying, were exhausted by means of sulphide of carbon, which dissolves only fatty matters, leaving a residue of pure alizarin. On removing the sulphide of carbon by evaporation there remained an oily, slightly reddish residue, a portion of which, when brought into contact with baryta-water, yielded at once, even in the cold, a barytic soap. Hence it is evident that the fluid in question contains a fatty acid in a free state. Another portion of this fluid was found to saponify very readily with hydrate of baryta, with the aid of heat, but there was left a non-saponifiable material, in all probability the same substance found by M. Weissgerber. The barytic soaps were readily soluble in alcohol, and separated therefrom in acicular crystals.

Since it is a well-known fact that sulpholeic acid, as obtained by the saponification of oils with sulphuric acid, when decomposed by means of water, yields a substance endowed with the property of rendering madder colours extraordinarily fast when mixed with mordants, it is very probable that the oleine of the Gallipoli acts essentially in producing such an organic mordant. The modified Gallipoli oil acts therefore—(1), as a mordant, because, according to the researches of Prof. Chevreul, some Turkey-reds contain only a very small proportion of alumina; (2), as fastener of the red lake; (3), it has been proved by Kuhlmann that it has the property of precipitating and energetically retaining several metallic oxides, as, e.g., oxide of iron. This may be readily proved by simply dipping previously oiled cloth into a solution of a per-salt of iron, to obtain, on dyeing it afterwards with madder, a beautiful purple colour.

That the peculiar action of the modified fatty substance is not simply confined to the red, but is equally strong for purples, is proved by the fact that the Messrs. Weber, at Mulhouse, used to manufacture a cloth, previously oiled and next mordanted, for purples, which was so fast that it could be plunged into rather concentrated hydrochloric acid without affecting the shade in the least. According to M. Persoz the most beautiful Turkey-red cloth exhibits, on being torn up, a nearly white section,—that is to say, the dye is rather superficial. His opinion is that the physical properties of the oil play some part in the process, inasmuch as it serves to envelope the particles of the lake, and to prevent the destructive action of externally applied agents. Resuming, in a few words, what may be considered experimentally proved concerning the action of the emulsified oil, it acts chemico-physically partly as a mordant, in as real a sense as alum; partly as a varnish, protecting as well as brightening the colour, the latter property being due to the peculiar transparency given to the cloth by the immersion in the emulsified oil.

We now return to the practical operations, and state first that this treatment of the cloth in the emulsified oil-bath, drying, and exposure to air, has to be repeated several times: a small piece may be taken for trying whether the oiling is sufficiently effected, by first working it about in a solution of carbonate of soda, and next immersing it in a bath containing a sumach infusion. If, on being removed therefrom and rinsed in cold water, the swatch assumes, when immersed in a solution of acetate of alumina, a deep yellowish tinge (isabella colour), the oiling is quite what it should be. After the oiling operation follows the removal of excess of grease, by means of a solution of carbonate of soda in water, whereby the unmodified oil is removed, as well as any excess of the modified portion which adheres only loosely to the fibre. The liquid remaining from this operation is usefully employed instead of the first oiling, and is therefore preserved and technically known by the name of old white bath. The operation which follows is that of applying the aluminous mordant, sometimes preceded by a bath containing an infusion of nut-galls and sumach; sometimes, again, the aluminous mordant and the astringent materials are mixed; but in all cases the mordanted cloth is dried, and after that passed through a tepid mixture of finely-ground chalk and water, in order thereby to aid the precipitation and fixation of the alumina. After rimsing and drying the cloth is ready for the dye-beck, wherein either madder or fleur de garance is used. In the former case chalk and bullock's blood, sumach and glue, are often added; but, the mineral matter excepted, there seems to be little use for these admixtures. Very frequently the dyeing operation is repeated twice, or even three times, with the understanding, however, that it is in each case first followed by a thorough clearing, next a fresh mordanting, and then again dyeing.

The clearing operation consists in boiling the dyed goods, under pressure, with soap and carbonate of potassa first; and next by a twice repeated boiling in solution of tin-salt and soap, or also, in addition thereto, carbonate of potassa. The chief action of these substances is, in this instance, confined to the elimination of the yellow and other colouring matters present in the cloth, which previous to clearing always presents a deep brownish brick-red, and lacks the peculiar beauty and the bleuctté appearance of genuine Turkey-red. The tin-salt acts undoubtedly, also, by causing the combination of a

small quantity of oxide of tin with the colouring matter, and thereby giving to the red a fiery-scarlet hue, which is one of the great characteristics of Turkeyreds dyed and well got up.

Among the modifications introduced in the above operations we briefly quote the following, reminding our readers, at the same time, that almost all dyers of Turkey-red follow processes of their own invention, and keep these modes of procedure strictly secret :- M. Haussmann pads the cloth in a mixture of olive oil and aluminate of soda, the effect of which is the simultaneity of the oiling and mordanting operations. M. Gastard applies-after every oiling, drying, and airing operation of the cloth—a nitric acid bath of 1'007 sp. gr. (exactly r per cent of the most concentrated acid), followed by drying in the open air: he appears to have been induced to this proceeding by the idea of promoting the oxidation of the oil. M. Steiner prepares the cloth,that is to say, causes it first to be padded in a solution of an alkaline carbonate; next it is put through the oil-bath, and thence it is passed between rollers along with two other pieces similarly prepared. On leaving the rollers the cloth is transferred to a stove-heated ageing-room, where it is placed in the best possible conditions for the rapid completion of the peculiar conversion of the oil without the necessity of repeating the operation. Very beautiful rose-red colours are obtained by placing previously oiled and feebly mordanted cloths along with Turkey-red pieces in the boiler, wherein the latter are placed for clearing under pressure. The colouring matter detached during that operation is sufficient to impart to the cloth, prepared as just mentioned, an excellent and fast shade. For purples it is required to use sheep-dung along with the oil-bath, and to employ nitro-sulphate of iron as a mordant. According to Kochlin the application of nut-galls or sumach is not required if the alum is first neutralised. The following may serve as a kind of diagram for the elucidation of this operation :- For 1000 kilos. of cotton* are required from 585 to 650 kilos. of the peculiar olive oil, 1500 litres of water, and from 9 to 10 kilos. of carbonate of potassa: after the immersion and working about in the bath the fabric is placed on a heap, in a cool place, † for ten or twelve hours, and next hung up to dry in a room heated to 60°. These operations are repeated from seven to eight times; next follows the washing in an aqueous solution of carbonate of potassa, consisting in a steeping of the goods during a period of twenty-four hours, and twice repeated in a solution of carbonate of potassa, sp. gr. 1'014 (containing about 2 per cent of that salt at 15° C.); wringing out, rinsing in cold water, and next padding, at 70°, in a bath made up of 300 litres of a decoction of nut-galls (10 kilos.) and 16 kilos. of alum, quantities which suffice for 500 kilos. of cotton; drying in the stove-heated room at 45°, being hung up there for two days.

Chalk Bath.—The dyeing is performed with 10 pieces at a time, with from 3 to 4.5 kilos. of madder for each piece; water, from 1500 to 1800 litres: the bath is gradually but regularly heated, during 21 hours, up to the boiling-point, at which it is maintained for a quarter of an hour. After this follows a second galling and mordanting, in the same manner just described, and after that again a dye-beck precisely similar to the first; followed by the first clearing, in a boiler under pressure, during eight hours, with 6 kilos. of soap and 1.5

^{*} This may be yarn, since it is very frequently dyed Turkey-red.

^{*} We may briefly point out the peculiar liability of Turkey-reds to spontaneous combustion.



MADDER.

kilos. of carbonate of potassa; second clearing, under pressure, with 6.5 kilos. of soap and 0.375 grm. tin-salt; next, third clearing the same as second; and next a bran-bath. The reader will readily observe that in the process as here described the oiled goods are not exposed to the bleach-field, and it is therefore apparent that the action of light can be replaced by that of heat. The oiled goods are sometimes heaped together in a room heated to 35°, care being taken to move the goods about so as to prevent their spontaneous combustion by a too active oxidation of the oil.

Turkey-reds are very readily recognised by the peculiar fiery and deep tone of the colour, but if there is any doubt on this subject it is only necessary to immerse the piece to be tested, for a few moments, in a boiling solution of



ARTIFICIAL ALIZARIN.

hypochlorite of soda, sp. gr. r·o36. No other red-dyed fabric will stand this treatment, whereas the Turkey-red becomes more fiery and but very slightly altered in depth. Add to this, that it is not affected in the least by being immersed in dilute hydrochloric acid and in a solution of oxalic acid. The pattern inserted at the top of the opposite page, for which we are indebted to Messrs. Steiner, Church, near Accrington, will give the reader an idea of what this dye is like when properly executed. It is dyed with madder root, not with garancin or any other special preparation.

For comparison we also annex a specimen of Turkey-red dyed with Messrs. Perkin and Sons' artificial alizarin, which we owe to the courtesy of Mr. W. H. Perkin.

This may also be the proper place to mention a new colour made known after the section on the coal-tar derivatives was completed. We refer to anthrapurpurin—the latest discovery of Mr. W. H. Perkin. This substance, which is already largely used by calico printers, has nearly the same affinity for mordants as alizarin, and the colours which it produces are analogous. With alumina it yields a red, and with iron mordants purple and black. In the tone of the colours thus produced there is a considerable difference, the reds being purer and less blue than those obtained from alizarin, while the purples are bluer, and the blacks more intense. In fastness against soap and light the colours are quite equal to those from alizarin. Its composition is—

Carbon	 	 	 	 65.62
Hydrogen	 	 	 	 3.13
Oxygen	 	 	 	 31.56
				T00'00

corresponding to the formula C₁₄H₈O₅. Anthrapurpurin, when heated, fuses, and then gives off orange vapours, which condense in yellowish-red leaflets or needles, though the largest part of the substance is carbonised. It is sparingly soluble in alcohol and ether, but rather more freely in glacial acetic acid. In water it is very slightly soluble. If heated along with zinc-powder it yields a hydrocarbon which agrees in its properties with ordinary anthracen. If an ammoniacal solution of anthrapurpurin is heated to 100°, in a sealed tube, for some hours, its colour changes from purple to indigo-blue. This solution, when acidified with hydrochloric acid, deposits a new product as a dark purple precipitate, soluble in ammonia and in carbonate of soda with a blue colour, but in caustic alkalies with a reddish purple. It dyes alumina mordants purple, and weak iron mordants an indigo-blue. It is probably isomeric with Stenhouse's purpuramide. Solutions of anthrapurpurin in caustic potash always show the absorption-bands in the same region of the spectrum, as do alkaline solutions of alizarin, but are less intense. The ammoniacal solution does not appear to give bands, nor does the ethereal solution of the colouring matter. In the latter case the violet is almost entirely absorbed.

A curious fact, and which may serve to illustrate the action of oils as mordants, is related in a Dutch work, very little known, published a few years since, on Borneo and adjacent islands. The authors, a party of an exploring expedition, found that whereas the very wild and barbarous tribes of a portion of the country in question were utterly ignorant of any art approaching to

the slightest degree even the knowledge of the Malays, concerning dyes and dyeing fabrics, they (the Dyaks of Borneo) were in possession of some very fast-dyed coarse fabrics, which were obtained by steeping the fibrous materials for some time in oil or fat, wringing out of the excess of these substances, and treading the greasy fabric about in the juice of some plants, or rather squeezing up with the feet the young leaves and twigs so as to obtain juice; after this another immersion in oil was resorted to, and again the squeezing operation just referred to; and lastly, after exposure to air, the fabrics were dyed a deep brownish-yellow by boiling them along with some vegetable matter, which, on investigation by the explorers (among whom were two physicians and a scientific chemist), proved to be simply an astringent which did not dye, but only slightly—yet not permanently—stained cotton or other fabrics not previously oiled. There is no doubt that the oil acts as a mordant in this case, and the treatment of treading the previously oiled cloth about in a vegetable readily-fermentable mass is, in all probability, done to cause the oil to undergo a peculiar change: the authors observe that, just as in Java, the inhabitants of the Indian Archipelago have in earlier times enjoyed a high degree of civilisation; they (the explorers) could not find out whether at any former time there had been intercourse between the Chinese and the aborigines alluded to; the Celestials are well enough acquainted with dyeing, and also that of producing a fast red, by means of chayaver.

We have now to say a few words about some products of the family of the Rubiacea, not used in Europe, but in some parts of Asia, as dye materials instead of madder, which does not thrive well in too hot climates. Some experiments for the cultivation of madder were made at the very extensive botanical gardens at Buitenhorg (Java), but it was found that unless the cultivation was proceeded with at a great elevation above sea-level, quite upon the high mountains, where European vegetables are purposely grown for the use of the Dutch colonists, madder did not thrive,—that is to say, the roots, although perfectly developed, did not yield any dye material worth mentioning, and the plant itself entirely degenerated. This has also been experienced at Pondicherry, and other parts of the mainland of India where the cultivation of madder was tried. We owe to the researches of Messrs. E. Schwartz and D. Keechlin some knowledge about the tinctorial products belonging to the Rubiacea grown in India (Southern Asia), samples of which were brought to Europe by M. Gonfreville.* Among these, in the first place, is the chayaver, a plant cultivated on the coast of Malabar and Coromandel, where the root is employed to impart a red dye to previously oiled cloth. This plant prefers a sandy soil; the root is very much like twine, exhibiting a greyish external colour, while its thickness does not exceed a millimetre. Internally its colour is bright yellow. This material is very tough, and far less easily pulverised than madder roots. The chayaver is a material very generally used as a dye throughout India; the chemical history and immediate analysis of this root are almost unknown. Dr. Schützenberger obtained a small sample, and by testing this he found that the chayaver contains chlorogenin and alizarin,that its colouring matter is readily exhausted by means of alcohol, owing to the natural acidity of the root, which does not contain lime salts. Messrs. Schwartz and Keechlin state, about this root, that they found it analogous to

Sec "Bulietin de la Société Industrielle," vol. v., p. 301, and following.

Avignon madder as regards its qualities as a dye-stuff, but being acid, as is the case with all the Indian Rubiacea in a very high degree, it requires the addition of chalk in the dye-beck; the colours produced upon fabrics are in every respect the same as those produced by madder, and are also the same with the same mordants. The chayaver, however, hardly contains the fourth part of colouring matter found in madder, taking, of course, equal weights of each.

Mungeet, or Rubia mungista, is characterised by the peculiarity that the stem contains more colouring matter than the root. In a dried state it is almost as rich in colouring matter as good Avignon madder, but it contains much acid and a great deal of yellow colouring matter; it does not yield fast shades at all, and, even with the treatment for Turkey-red, the cleared redat first bright and beautiful-is rapidly destroyed by sunlight. Dr. Stenhouse* has made some researches on this mungeet which prove that it does not contain alizarin or purpurin, but a peculiar colouring matter which this chemist has called mungistin. To obtain this, the previously pulverised root is treated with a boiling solution of alum (500 grms. of mungeet root, I kilo. of alum, and 8 kilos. of water); the liquid, having been filtered, is boiled, when there is thrown down a bright red precipitate, which is collected on a filter, washed, and dried. The dried material is treated with sulphide of carbon, which dissolves the colouring matter, while a resinous substance is left. The sulphide of carbon solution yields, on evaporation, a bright red residue, consisting of mungistin and purpurin. When this is acted upon by boiling water acidified with acetic acid, the purpurin is left undissolved, while the mungistin is taken up, yielding a yellow solution as long as the fluid is hot, but on cooling the mungistin is thrown down. This precipitate is purified by means of boiling alcohol, from which the mungistin crystallises out on cooling. This substance is sparingly soluble in cold, but more freely in hot, water; slightly soluble in cold, but readily so in boiling, alcohol. Mungistin is fusible by heat, and crystallises again on cooling: it dissolves in aqueous solutions of the carbonates of potassa and soda, and the caustic alkalies and ammonia, yielding bright red solutions. With baryta water it yields a yellow precipitate, and hydrate of alumina forms with it a bright orange lake. Mungistin is soluble in strong sulphuric acid; its formula is, according to Dr. Stenhouse, C₈H₆O₃: concentrated nitric acid converts mungistin into phthalic and oxalic acids; highly concentrated ammonia converts this body into a brownish humuslike substance.

Under the name of nona is designated the root of a rubiaceous tree belonging to a species of guilandina. This root has great similarity with madder root, but is more difficultly pulverised, and contains a large quantity of yellow colouring matter and much acid, so that previous to being fit for dyeing it should be washed with water, and in order to render the colours fast carbonate of soda is required to be added to the dye-beck. According to the experiments made by Messrs. Schwartz and Kæchlin, the nona root should be first ground to a fine powder, next washed with fifty times its weight of pure cold water, after which it is fit for the dye-beck, with the addition of one-fifth of its weight of carbonate of soda. The initial temperature should be about 39°, and gradually be raised to boiling: in this manner previously oiled and mordanted cloth

^{*} See "Annalen der Chemie und Pharmacie," vol. cxxx., p. 325.

cleared after dyeing, as described for Turkey-reds, becomes beautifully scarlet, very nearly equal to good Turkey-red. Cloth not oiled, simply mordanted in the ordinary manner for red madder shades, is dyed, by the aid of nona, somewhat like madder but more yellowish, and this tinge remains after clearing.

The dye material known as ouongkondou contains, according to the researches of the chemists just named, about from one-third to one-half of the quantity of red colouring matter found in good Avignon madder, but the ouongkondou, although less acid than mungeet, yet requires in dyeing an addition of 3 per cent of carbonate of soda. The shades obtained are less fast and less beautiful than those yielded by nona.

Hachrout is, if not identically the same as nona,—which may be the case considering the large number of dialects and different languages spoken in India,—at least so very similar thereto that Messrs. Kæchlin and Schwartz detected no difference.

The horticultural experiments made with these plants in Java, by the care of the directeur des cultures in that island, prove that, with suitable nursing and careful selection of manures and soils, the plants are very greatly improved in their qualities as dye materials. The Javanese have discontinued the use of these materials, because the European trade imports to them far better goods and far faster dyed fabrics than they could manufacture, and at far less cost.

The scientific researches on these substances are very incomplete; there are in the India Museum, formerly open to the public, when at old Fyfe House, now at the India Office, a very large and interesting number of samples of various dye materials used all over India by the natives. It would add much to our knowledge on this subject were some scientific chemist, who has time and leisure, supplied with a sufficient quantity of all or some of them to complete an investigation into their properties.

CHAPTER IV.

RED WOODS.

A. Open or Soluble Class.

SEVERAL woods are known, all characterised by the feature that they impart to tissues mordanted with alumina or tin a fugitive red colour. The trees from which they are obtained belong to the natural order of Leguminosæ, and are natives of warm climates, especially Central and South America, the Antilles, and India. These woods are met with in commerce in the shape of fagots, of irregular blocks, and billets. In physical structure these woods are hard and compact; the colour is internally bright yellow, but the portions exposed to air are brown. They are devoid of smell; their taste is sweetish bitter or astringent, and they tinge the saliva red. In India some of these woods were employed for dyeing purposes long before the discovery of America (1492), and some of them even appear to have been known and used in Europe before that epoch. The following varieties of "open" red woods are used to a greater or less extent:—

1. Fernambuco* wood, the best variety and the richest in tinctorial matter, is imported from Paraïba. It is the product of the Cæsalpinia crista, a tree abundantly found in Jamaica as well as in Brazil. It is imported in billets, varying in weight from 4 to 120 lbs. The wood is hard, heavy (the sp. gr. of these woods being generally above that of water, and averaging 1°014), compact; externally red; internally pale yellowish red when freshly cut, but on exposure to air it becomes a deep brown-red. Its taste is sweetish, and its odour faintly aromatic. It tinges water beautifully red.

2. Brazil wood, properly so-called, the product of the Casalpinia brasiliensis, from the immense forests of that large country, is met with in trade in the shape of large irregularly hewn blocks; it is hard, compact, and, when freshly cut, a brick-red, but becomes deeper brown on exposure to air. It is capable of taking a polish. Its tinctorial value is about one-half less than that of Fernambuco wood, but like most of these woods improves by age. It becomes better even after having been cut down, provided it is not exposed to excessive moisture.

3. St. Martha wood, produced by the Cæsalpinia echinata, growing in the native forests of St. Martha, or Sierra Nevada of Mexico. It is met with in commerce in billets about I metre in length; one end of these is commonly cut off rounded, but the other end is sawn through square. These billets are full of cracks, generally filled with splinters, and vary in weight from 20 to 40 lbs. Its physical properties are much the same as those of the kinds above

^{*} Also written Pernambuco.

mentioned. Its transverse section exhibits a starry form; its tinctorial value is less than that of genuine Fernambuco wood, but it is generally considered the second best for dyeing purposes.

- 4. Nicaragua wood is probably the produce of the same tree as the lastnamed species. It is named from that region of Central America where it grows.
- 5. Sapon, or sappan, wood is the product of the Casalpinia sappan, a tree growing over a considerable portion of the warmer regions of Asia. This wood occurs in commerce in the form of billets, free from splinters, and exhibiting a medullary cavity, sometimes filled with a reddish yellow pith, but sometimes quite empty. The wood is very hard and compact, fine grained, capable of a brilliant polish, while its colour is less deep than that of most kinds of these woods. Two principal kinds are known, viz., that imported from Siam, in pieces free from splinters, and of the thickness of a man's arm, the colour being rather deep red internally; the other variety is known as Bimas, and occurs in sticks of from 27 to 33 millimetres thickness; internally its colour is yellowish, but where it has been exposed to the action of the air it is rose-red. The so-called Lima wood of commerce is a variety of sapan, and the dye-woods imported from Manilla and the other Philippine Islands, from St. Martin and Padang (Sumatra), are inferior qualities of the same.
- 6. Bahamas, or Jamaica wood is, according to some, the product of the Casalpinia vesicaria; but, according to others, is yielded by a shrub belonging to the genus Balsamodendron. It is known in trade by various names according to the place from which it is shipped, among which is Nickérie, Surinam, and especially the Island of Jamaica. It is met with in the shape of sticks, free from bark, and about 54 millimetres thickness, covered by whitish splinters. Within its colour is red-brown with darker veins. It is the lowest in tinctorial value of all these woods.
- 7. Californian wood, the product of a hitherto unspecified Cæsalpinia, found in the Californian forests, is as yet only met with in trade in the shape of irregularly-sized knotty pieces. It is exceedingly hard, its colours rather dark yellow when freshly cut, becoming first brown on exposure to air, and, lastly, violet-red.
- 8. Tierra Firma wood, the product also of an unspecified kind of Cæsalpinia, growing in some of the forests of Venezuela and New Granada. It occurs in the shape of hewn blocks, serving for stowage, and is very hard, knotty, and compact, with longitudinal fibres. It is internally of a golden-yellow, exhibiting concentric circles of a yellowish red.
- 9. Bahia wood, so-called from being generally met with in the forests of the Brazilian province of that name, occurs in large square billets. Its colour is yellowish, but becomes darker on exposure to air. In tinctorial value it holds about the middle place between the best Fernambuco and the inferior varieties mentioned above.

The chemical history of these red woods is as yet in a very incomplete state. Nothing is positively known about the foreign substances occurring in the wood along with the colouring matter, and that substance itself has been but incompletely studied. As far as the former are concerned, we may reason by analogy and say that these woods contain saccharine matters,

astringent principles, organic acids combined in various ways, resins, and mineral salts.* Hitherto only one colouring matter has been found in these woods, but the absence of others, however analogically probable, is not formally demonstrated. The colouring material is totally soluble in water, and can be extracted from the ligneous matter by repeated decoctions or infusion. It exists in the wood in an almost colourless state, or at least its colour is only a pale yellow, but on coming into contact with air this hue becomes gradually darker, and at last red-brown. There appears to be slow oxidation of colourable matter to form a real pigment. The aqueous decoctions of these woods are yellow at first, and only assume a red by the action of air or the addition of aërated water (that is, ordinary fresh water, which, not having been boiled, contains air). This phenomenon, however, is somewhat dependent on the variety of the wood, and also on the fact of its more or less immediate use after being ground to powder. The colouring matter is supposed by some to exist in these woods as a glucoside, since the decoction exerts very little reducing action upon a cupro-potassic solution; but when the decoction has been heated for some time with either sulphuric or hydrochloric acids it yields, on treatment with the cupro-potassic test, an abundant precipitate of red oxide of copper. After the splitting-up of the glucoside has been effected the colouring matter exhibits a tendency to crystallise, which it did not previously possess. It is only required to treat the acidified decoction while yet hot (that of acid is sufficient) with an alkaline salt, when, on cooling the fluid, there will appear a more or less red-coloured crystalline substance, its shade depending on the degree of oxidation it has undergone. The addition of the alkaline salt has the effect of diminishing the solubility of the colouring matter. There exists, therefore, in the decoctions of the woods a colourable glucoside in a more or less advanced state of oxidation; and, moreover, a certain proportion of free colouring matter, which either preexists as such in the wood, or is formed during the boiling with water by the splitting-up of the glucoside.

The colourable glucoside, which is very abundantly present in freshlymade decoctions of the wood, is not precipitated by neutral acetate of lead, but is thrown drown by the subacetate. When a solution of the neutral acetate is added to a decoction there is formed a bulky brick-red precipitate, which contains, besides tannin and some foreign substances, chiefly bresiline and colouring matters already oxidised. The filtrate from this precipitate, a faintly yellow liquid, dyes up shades of equal richness, but of far more beauty than the original decoction. This liquid, moreover, yields, on being treated with basic acetate of lead, an abundant lilac precipitate. Oxidation of the colouring matter is a slow process in the first place, and requires especially conditions which favour it, and among these ammoniacal vapours and the faintest traces of potassa or soda are the chief agents. Decoctions of most of these woods may be kept even in open vessels for several months without any very prominent change being observable. The colour of the liquid remains bright yellow, while the rasped wood becomes rapidly brown, an effect, as regards the latter, due to the presence in the wood of substances

^{*} Generally speaking our knowledge about wood is very limited, and it is to be regretted that the wares here named have not been more fully studied. They deserve it equally with such kinds of wood as chony and iron-wood, and many others, the products of warmer climes.

which aid the oxidation by becoming altered somehow themselves. To a certain extent the wood, after having been rasped, gains in tinctorial value by contact with air for some time, but it should not be exposed too long, and certainly not be submitted to the direct action of the sun's rays, which will soon cause the destruction of the pigment altogether. The decoction of the red woods is also very sensitive to the action of reducing agents; sulphuretted hydrogen discolours this liquid, and when boiled even with Thomath of sulphide of sodium, the decoction only exhibits a reddish hue due to the influence of the alkaline reaction of the salt, but this colouration disappears if the alkali is neutralised by an acid. When a decoction so treated, and quite colourless, is used for a dye-bath, it would at first appear to be worthless, but as the temperature rises the colour returns, and the dyeing operation goes on as well as with the original decoction though attended with a great loss of colouring matter. Acids have the effect of rendering the colour of the decoctions yellow, with a more or less orange shade, which depends on the fact of the more or less oxidised state of the wood used for the decoctions. After the lapse of some time decoctions so treated deposit a crystalline substance, which is yellow in case the decoction was quite deoxidised, otherwise it exhibits a red colour. Excess of hydrochloric acid added to the decoction turns them a bright rose-red, but this hue disapears on the addition of water. Caustic and carbonated alkalies turn the colour of the decoction to a carmine-red. When lime or even chalk is added to a decoction of these woods the liquid becomes carmine-red coloured: this base has a specific effect in promoting the oxidation of the decoction. The liquid thus treated soon becomes covered with a black pellicle, which after a while sinks to the bottom of the liquid, and the formation of another coating in its stead begins. Alum turns the decoction to a red, but does not cause a precipitate; if, however, so much of an alkaline carbonate is added as to make the alum basic and a gentle heat is applied, a red-coloured lake is precipitated. Acetate of alumina heated with the decoction behaves in the same manner. Neutral acetate of lead yields merely a slight reddish precipitate. When the substance thus thrown down is removed from the fluid by filtration, the filtrate is found to be as fit for dyeing and even to give better and brighter colours than the primitive liquid. Hence it appears that neutral acetate of lead precipitates only the super-oxidised matters, and, moreover, removes from the decoction such compounds, tannin, for instance, as may affect the purity and brilliancy of the dye. Subacetate of lead yields a very abundant precipitate of a bluish colour; the filtrate from the liquid so treated does not contain anything worth attention. Nitro-muriate of tin yields with the decoction a red precipitate, which turns to a carmine-red of the greater beauty the less the liquid was previously altered. The characters here described are those which M. Persoz obtained while experimenting upon decoctions of Bahia wood both old as well as freshly made.

M. Girardin's experiments on this topic differ in some particulars, but it ought to be observed that in the first place the time elapsed since the rasping of the wood has some influence, and, secondly, the different kinds of these woods as met with in commerce may, and undoubtedly do, exhibit slight differences when the decocions are tested with reagents.

Brazil wood decoction is better fit for dyeing when it has been kept for a good length of time in a cool place than when recently made. This fact,

well known to all dyers, may be explained by the slow alteration and decomposition of substances present in the decoction which affect the purity of the hues; it is, moreover, possible that the colouring matter becomes reduced by a special fermentation.

Dr. Dingler* has made known a simple method for purifying from the yellow colouring pigment the decocions made with some of the inferior woods, viz., Bimas, Santa-Martha, Aniola, Nicaragua, Siam, and Sappan varieties, which by this method are as excellent for dyeing as the best Fernambuco wood. It consists in adding to the boiling liquid wood and small quantities of very carefully skimmed milk. The coagulation of the casein causes the precipitation of the yellow colouring matter along with the casein. Gelatin also may be applied for the purification of the inferior qualities of these woods. If the shavings or raspings of the woods are moistened with water containing 2 kilos. of gelatin to the half heccolitre, and the mass left for some days heaped together, the wood yields better results in the dye-beck, because the colouring matter is rendered more readily soluble, while the effect of a moist fermentation, which as observed by M. Leuchs, greatly improves some kinds of these woods, may in the case mentioned have something to do with the improvement of the quality.

The colouring glucoside of Brazil wood is only imperfectly known. According to Dr. P. Schützenberger's experiments, it is a non-crystallisable substance soluble in water in every proportion, and also in alcohol. Its taste is bitter or sweetish; its colour is a beautifully bright yellow when the substance has not undergone any change. This glucoside may be obtained by concentrating the decoction in vacuum at the ordinary temperature of the air to one-tenth of its original volume (sp. gr. 1.075), and then adding either sulphate of soda or common salt. It is thereby precipitated in the shape of a pasty mass completely soluble in pure water. The ordinary commercial extracts of the red woods (their sp. gr. varies from 1.075 to 1.162) yield, on the addition of water, a yellowishcoloured flocculent precipitate, which would make it appear that the colouring matter is more readily soluble in a concentrated than in a more dilute liquid, but this reaction is explained by the partial decomposition and oxidation the glucoside undergoes while the preparation of the extract is going on. The product of the splitting-up is kept in solution owing to the state of concentration, and by the aid of the saccharine matters present in that solution, and the precipitation of the more or less modified glucoside, is due to the fact, that on the dilution of the extract with water the solvent influence of the other substances is decreased.

By the name of bresiline is understood the free colouring principle disengaged from its glucosic combination. Bresiline was first studied and isolated by M. Chevreul,† who obtained it by the following process:—The wood, previously ground, is exhausted with water, and the fluid obtained is evaporated to dryness on a water-bath; the dry residue is taken up by water again, and the fluid shaken with some hydrated oxide of lead, in order to saturate the acids present; the liquid is next filtered, and then again evaporated to dryness, after which the residue is taken up by alcohol; this solution is first somewhat

^{*} See "Annales de Chimie," vol. xvii., p. 323. Dingler's "Polytechnisches Journal," vol. xxv., p. 80.

[†] See "Annales de Chimie" (first series), vol. lxvi., p. 225.

concentrated by evaporation, next water is added, and it is then treated with a solution of gelatin to remove tannic acid; after filtration the fluid is again evaporated to dryness, and the residue afterwards treated with boiling alcohol. On cooling the bresiline is deposited in a crystalline state. It often happens that in old decoctions of these woods (even when their sp. gr. is as low as from 1.010 to 1.014), which have been kept for a long time in contact with air in a cool place, an abundant deposit of bresiline in a crystalline state is found at the bottom of the casks. Dr. Bolley has had an opportunity of fully investigating this material, which was given to him by Messrs. Muller, of Basel.* Dr. P. Schützenberger states that he also obtained from the same parties a sample of this spontaneously-formed crystalline deposit; on treating it with boiling alcohol, and evaporating it without the contact of air and light, amber-yellow crystals of pure bresiline are obtained. The shape of these crystals is that of hexagonal or klinorhombic prisms; they are soluble in water, alcohol, and ether; the colour of the aqueous solution is slightly more reddish than that of the alcoholic. Even the smallest trace of ammonia is sufficient to turn these solutions intensely carmine-red. When the crystals are kept in well-closed bottles they become darker, especially on that part of the bottle which is most exposed to light. This is probably an effect of oxidation favoured by the action of the light. When the alcoholic solution of bresiline is preserved for a length of time, or is evaporated, especially if slowly, it deposits, in addition to the yellow bulky crystals of bresiline, small scaly crystals exhibiting a greenish cantharides-like reflection. This substance, which contains nitrogen, is probably formed under the combined influence of ammonia and oxygen. The crystals of bresiline are anhydrous, and become decomposed when heated to from 130° to 140°.

According to the analyses of Bolley and Greift, the formula of this substance is $C_{22}H_{20}O_7$. As deposited from ordinary alcohol, which always contains water, bresiline is obtained in the shape of golden-yellow crystalline needles felted together; this form belongs to the monoclinic system, and these crystals contain 2 molecules of water of crystallisation, formula $C_{22}H_{20}O_7+2H_2O$. This water is driven off at 80° C. Dr. Bolley has not been enabled to obtain any substitution compound by means of which this formula might be controlled; he states, however, that bresiline combines with bisulphite of soda, yielding a colourless crystalline product: by this reaction bresiline ranges with the aldehydes.

Dr. Schützenberger states that on heating pure bresiline and anhydrous acetic acid to 140° he obtained a derivative insoluble in water and crystallising from its alcoholic solution, forming bright yellow needles. Since bresiline is thus acted upon by anhydrous acetic acid and combines therewith, it behaves as an alcohol, and is in all probability therefore a polyatomic alcohol. Bresiline heated along with ammonia to 100° in a sealed tube and without excess of air, yields an amidated colourless compound, which is very prone to decompose in contact with air, and is a true base.† In this respect bresiline is quite similar to the hæmatoxylin found in logwood; indeed the formula given

^{*} See Bolley and Greift, "Schweizerische Polytechn. Zeitschrift," 1864, vol. ix., p. 134.

[†] Schützenberger and Paraf, "Bulletins de la Société Industrielle de Mulhouse," vol. xxxi., p. 50.

by Bolley for bresiline leads to the conclusion that bresiline and hæmatoxylin only differ by the elements of phenol—

Some authors hold the opinion that bresiline and hæmatoxylin are identical, but though there exist a great analogy between these substances they are not identical, as is proved, moreover, by practice on the large scale as well as by recent chemical researches. Hæmatoxylin when acted upon by nitric acid yields only oxalic acid, whereas bresiline under the same conditions yields trinitro-phenic or picric acid. Brazil wood, or the colouring matter contained therein, is employed in dyeing in the following conditions:—

r. The wood itself, either reduced to shavings, raspings, or powder, serves for the production of red, rose-red, amaranth colour, and carmine-red; sometimes the wood is mixed in smaller or larger proportion with garancin for the dyeing of the so-called garancin colours. The wood is used in a mechanically divided state for the preparation of the decoction and concentrated extracts.

2. Decoction, or liquor of Brazil wood, obtained by boiling by means of steam the raspings of the wood with from 18 to 20 times its weight of water, or by the exhaustion of the wood by displacement with boiling water. This liquor is used for dyeing, for the preparation of concentrated extracts, and for the manufacture of the Brazil lakes.

3. The concentrated extracts having a sp. gr. of 1.075, 1.116, 1.162, or even evaporated down to solidity. In these states the dye is more convenient for carriage, whence the employment of such extracts is rather increasing. The mode of preparation of these and similar extracts will be fully described in a separate chapter. It need hardly be said that the quality of these extracts varies greatly, not only in respect of the richness of the colouring matter therein contained, but also as regards the purity and freshness of the shades produced; these differences depend partly upon the kind of wood used, and partly also upon the care taken to prevent oxidation during the process.

4. Lakes, of which there are a great variety, made with Brazil wood, known commercially by various names, as, for instance, Venice ball lake, Vienna, Florentine, Berlin, and New lakes; they are chiefly used for the preparation of coloured paper, for printing paper-hangings, and by artists, decorators, and carriage painters. The mode of manufacture of these and other lakes will also occupy our attention more fully hereafter.

Bresiline belongs to that class of pigments which cannot be fixed upon any kind of textile fibre, except by the aid of a mordant, which, in this instance, just as in the case of madder, not only fixes the pigment, but also determines and develops the shade. With a piece of cotton previously mordanted with alumina, hydrated oxide of iron, or a mixture of the two, we obtain with bresiline, or any preparation of Brazil wood, colours which to some extent resemble those produced by madder, or rather by cochineal. The alumina mordants will produce red or rose-reds; the iron mordants, a greyish violet or black; the mixture of alumina and iron mordants yields a brown. Binoxide of tin again yields red; the black is nothing very particular; the violet absolutely ugly; the reds and roses are temporarily brilliant, but soon become dull, and

disappear by the action of light. Hydrated oxide of chromium yields an olive colour. All these colours are characterised by their looseness, and by being readily affected by all kinds of reagents; they do not stand soaping, or even ordinary washing with soap. The Brazil wood reds are rendered a violet-blue by alkalies, while acids turn them yellow.

In calico dyeing and printing the red woods are used in connection with garancin, as well as for the purpose of sightening the mordants temporarily. The decoctions and extracts are frequently used for producing steam-reds: the properly thickened liquor is mixed with—(I), acetate of alumina; (2), protochloride of tin and oxalic acid; (3), a salt of copper (chiefly the acetate), destined to promote oxidation during steaming. A good steam-red can be made with a mixture of Brazil wood liquor with chloride of aluminium and chlorate of potash. The chloride of aluminium is decomposed by drying, and hydrochloric acid is given off, which reacts on the chlorate of potash, liberating chloric acid, which oxidises the colouring matter, the ultimate result being a compound of alumina with oxidised colour. This red is very fast. These steam-colours contain, therefore, in solution all the materials required to form a red lake, which, by the steaming, is precipitated as well as fixed upon the fibre.

The following are some of the reds and rose-reds used for steam and spirit colours upon calico:—

Deep Red for Machine-work and Steaming.—9 litres of a decoction of St. Martha wood, sp. gr. 1.022; I litre of berry liquor, sp. gr. 1.060; 1.5 litres of red liquor; 1.5 kilos. of starch; 125 milligrms. of a solution of nitrate of copper, sp. gr. 1.532.

Steam Rose-Red, upon Previously Mordanted Cloth.—2.5 litres of liquor, sp. gr. 1.022; 5.5 litres of water; 3 kilos. of gum; 300 grms. of solution for rose-red (see immediately below); 50 grms. of nitrate of copper, sp. gr. 1.618.

The Tin Solution for Rose-Red is made up of—12 kilos. of nitric acid, sp. gr. 1'334; 3'25 kilos. of water; 1'25 kilos. of sal-ammoniac; 2'5 kilos. of bi-chloride of tin; 1'5 kilos. of pure tin (either Banca or Cornish).

Spirit-Red.—5 kilos. of decoction of St. Martha wood, sp. gr. 1.022; boil therein 0.25 kilo. of gum tragacanth, and add 600 grms. of bichloride of tin, sp. gr. 1.532; 180 grms. of salt for rose-red; 150 grms. of nitrate of copper, sp. gr. 1.532; 2.1 kilos. of tin solution as for rose-red. This colour is not to be steamed, but becomes fixed by keeping the cloth hung up in a suitable room.

Spirit-Rose is made up of 1 kilo. of the red mixture above mentioned and of 1.5 kilos. of gum tragacanth water. It is usual to apply a mixed mordant for these colours,—that is to say, tin and alumina mixed, or each of these separately; oxide of tin yields better colours on cotton than alumina.

Woollen tissues which are to be dyed with red woods are first mordanted with protochloride of tin or an aluminous compound. For a quantity of 10 kilos. of wool, 1 kilo. of cream of tartar and 2 litres of a so-called red solution are taken; the wool is put in this mixture, and kept boiling for an hour. The red solution consists of 8 litres of water, 400 grms. of common salt, 1.25 kilos. of tin, and 8 litres of nitric acid. The alum-bath suitable for 10 kilos. of wool consists of 2 kilos. of alum and 20 grms. of sulphuric acid. The woollen goods are left boiling an hour.

The employment of the red woods, at least for the production of red steam-

colours upon wool and silk, and even for dyeing, has been in some cases superseded by the new aniline colours, but they are used for clarets and browns along with orchil and other colouring matters. They are also largely used in dyeing so-called "mock crimsons," in imitation of those produced with cochineal. In scarlet and crimson coburgs, and other mixed goods, the cotton warp is got up with a wood of this class in conjunction with a per-salt of tin. The best method of testing the woods, or the extracts thereof, for their value is a mode of assay founded upon either a dyeing or printing process, conducted as follows:- Take 10 grms. of the material to be tested, if wood it must be previously pulverised, and also a piece of 25 square centimetres of cotton cloth, mordanted, as indicated above, for testing garancin; put these materials into a suitable glass vessel, wherein is poured 1 litre of water; heat the vessel in a water-bath, and keep the dyeing process up for half an hour, care being taken to stir the contents of the vessel about with a glass rod. The pattern, after having been washed with cold water, is placed for some time in a bran-bath, at 80°, and afterwards again washed with cold water, and dried. This mode of testing requires the use of a standard sample for comparison.

Commercial samples of ground woods often contain an excess of moisture. If on drying at 212° F. the loss exceeds 32 per cent, there is good cause for complaint. If allowed, when very moist, to lie long in large heaps, heat is developed, and the colouring matter is gradually destroyed. The extract, at 10° Baumé (sp. gr. 1'075), is about five times as strong as the wood.

If preferred, the following colour mixture may be made up:—Extract of the wood, 20 grms.; alumina mordant, 200 grms.; water, 140 grms.; pulverised gum, 160 grms. After the latter substance has been dissolved the fluid should be passed through a fine sieve. This mixture is printed on by means of a roller; if calico, by means of block-printing; if muslin is the fabric upon which it is desired to test, after drying the fabric so treated is steamed and washed. This assay also requires a standard sample of extract.

The red dyes produced by these woods or extracts, and fixed upon fabrics, are recognised by the following tests:—Like the reds produced by madder and cochineal, they are destroyed by chlorine and hypochlorous acid: on incineration they leave a compound of alumina or tin, according to the mordant employed; but the reds produced by the woods are also destroyed by boiling soap solution, which distinguishes them from madder reds. When successively immersed, first in hydrochloric acid, and next in lime-water, the red wood shades are turned violet, which is destroyed by boiling soap solution. Concentrated sulphuric acid turns the red of the woods to deep cherry-red, while it converts cochineal to an orange-yellow.

B. Close or Insoluble Class.

The principal woods of this class are santal wood, cam wood, and bar wood. These woods are of a more resinous character than Brazil wood and its allies, yielding faster dyes, but from the insolubility of the colouring matters they cannot be used in the state of extracts.

Sanders Wood, Santal Wood, or Red Sanders.

This wood is the product of *Pterocarpus santalinus*, a tree growing in India, Ceylon, Timor, and other tropical parts of Asia. The wood is hard, of a

high specific gravity, viz. 1'014, very dry and compact, of a blackish-brown colour externally, while within it is red. The fibres of this wood occur alternately in layers running in opposite directions; as a consequence thereof, when an attempt is made to plane it, it will exhibit alternately a polished and a rough torn-up surface. For dyeing purposes the old wood is the best, because it is richer in colouring matter.

Santal wood is met with in commerce in the state of a powder specifically lighter than water, with a smell like that of orris-root: its taste is somewhat aromatic. This substance contains pigment, gummy and astringent matters, chloride of calcium, sulphate of lime, chloride of potassium, organic potassa salts, phosphate of magnesia, alumina, oxide of iron, and silicic acid. The colouring matter of santal wood is insoluble in cold water, very slightly soluble in boiling water, readily soluble in alcohol, ether, acetic acid, and caustic

alkalies, and precipitable from its solution therein by an acid.

The chemistry of this product is by no means quite complete. Pelletier was the first who discovered and isolated santalin as a red resin, the solubility and properties of which are those above described. Meier prepares santalin by treating the wood with ether; the concentrated solution yields the substance in a crystalline yet impure state. These crystals are first washed with water, and next re-dissolved in alcohol; the alcoholic solution is precipitated by acetate of lead, and the ensuing precipitate washed with boiling alcohol, and next decomposed by means of sulphuric acid in the presence of alcohol. After removing the sulphate of lead, the previously concentrated alcoholic solution deposits santalin, in the shape of small crystals, of a beautiful red colour, fusing at 104°. Dr. Dussauce's plan of preparing santalin is by precipitating the alcoholic extract of the wood by means of hydrated oxide of lead. After washing, the precipitate is dissolved in acetic acid, and to this solution a large quantity of cold water is added, which indeed precipitates the colouring matter, but in a rather impure state, since the dye thus obtained does not yield good results.

Santal Wood contains on an average about 16 per cent of santalic acid. According to the researches of Weyermann and Hæffely the composition of santalin is $C_{15}H_{14}O_5$. This result was controlled by the analysis of a baryta salt of santalin, obtained in the shape of a violet crystalline precipitate by adding chloride of barium to an ammoniacal solution of santalin: the formula of this compound was found to be $C_{30}H_{26}BaO_{10}$. Dr. Bolley considers that santal wood contains two different colouring matters, one of which is richer in oxygen but poorer in hydrogen: this is the material occurring in the old dark-coloured wood. The other is found in the younger and paler variety. According to the researches of Meier and Wimmer santalin is accompanied by divers red and brown coloured matters, more soluble in water than santalin itself and the products of its oxidation. This assertion is certainly substantiated by the fact that the young twigs of the *Pterocarpus santalinus* are internally yellow-coloured, and only become red by the action of the air.

Santalin exhibits the following properties:—It is a beautiful red crystalline powder, almost insoluble in water, soluble in alcohol, ether, and acetic acid: the colouring matter is very readily withdrawn from the acetic acid solution by albuminous substances, which retain it energetically; alkalies dissolve santalin, yielding deep violet-red solutions, from which it is thrown down unaltered by acids. Santalin fuses at 104°.

According to Prof. Girardin, the alcoholic tincture of santal wood exhibits the following reactions:—Addition of water causes a yellow turbidity; with alkalies the colour turns carmine; lime-water produces a reddish-brown ochreous precipitate; protochloride of tin a blood-red precipitate; bichloride of tin a brick-red precipitate; per-salts of iron a red-brown precipitate; salts of lead a violet precipitate; corrosive sublimate a scarlet precipitate; salts of silver a red-brown precipitate.

Santal wood is used for some peculiar red shades upon wool and cotton after having been mordanted with alumina or oxide of tin, and also as a bottom for the so-called Nemours or "national blue" upon wool. Mixed with other dyes, it is used for the production of brown, bronze, and olive colours. Santal wood dyes wool permanently, even without the aid of any mordant.

The following woods met with in commerce belong, as far as is known, to the same category as santal wood:—

Caliatur or Cariatur Wood is imported from India in blocks of from 2 to 3 metres in length; it is a hard, compact, and imperishable wood, internally bright red, and is superior to santal wood as a dye-stuff, but is rather expensive, and is rarely used.

Madagascar Wood is of a wine-red colour.

Barwood may be considered as the type of the insoluble class of red woods. It is obtained from the west coast of Africa, especially from Sierra Leone and Angola. The botanical name of the tree is Baphia nitida, which, singularly enough, is also said to yield camwood. In the log barwood is compact, and has an orange colour when polished. When rasped-the state in which it is generally met with in trade-it is a rough, harsh, red powder, without smell. Cold water, after maceration for five days with the ground wood, acquires merely a pale fawn-colour, about 0.85 per cent only of colour being taken up. Boiling water takes up about 7 per cent of colour, which on cooling is almost entirely re-deposited as a reddish powder. Hence all attempts to prepare from it a liquor or extract fit for use in dyeing and printing have failed. In alcohol the tinctorial principle is more soluble, but it is only by repeated treatment with boiling spirit that the wood is entirely exhausted. The amount of colouring matter is high, averaging 23 per cent. In caustic soda and ammonia it dissolves with a violet-red hue, and is re-deposited on neutralising the liquor with an acid. An attempt has been made to utilise the solvent power of alkalies in order to obtain an extract, but the brightness and permanence of the colour are so much impaired that the process is of no practical value. Acetic acid extracts the colour, and becomes of a dark brown hue, but if this extract is mixed with water it dyes very flat and meagre shades.

The alcoholic solution gives the following precipitates:—With proto-salts of iron, a violet; with salts of copper, a brownish-violet; acetate of lead, a deep violet; chloride of tin, a light red; sulphate of zinc, a bright red; tartar emetic, a cherry-red; nitrate of bismuth, brilliant crimson; corrosive sublimate, a brick-red.

Barwood is very extensively used in producing upon cotton-yarn the well-known "barwood red." This is a shade much more permanent than any obtained from the soluble red woods, and is used as a cheap substitute for Turkey-red. The cotton is first well mordanted with an astringent,—generally

sumach,—and with "barwood spirit," a preparation of tin, receipts for which will be given in a special chapter. It is then boiled along with the loose wood. This process presents two interesting peculiarities: absolute contact between the ware and the mordanted goods appears necessary, and, unlike ordinary cotton-dyeing operations, it is carried on at a boiling heat. A reduction of temperature is fatal to a good result.

Cam Wood or Kambe Wood.—This dye ware is brought from the Gaboon and Sierra Leone. It yields its colouring matter to water much more freely than barwood and sanders, but is still not sufficiently soluble to produce an extract. The shades which it yields are, under all circumstances, more yellow than those produced by Brazil wood. It is used by woollen dyers to produce certain fast reds, maroons, and especially browns of a very permanent character. It also serves as a ground or "bottoming" for certain blues, whether produced with the vat, extract of indigo, or with anilines, especially Guernsey blue.

Logwood, or Campeachy.

Logwood, Campeachy wood, called formerly "blue wood" and "black wood," is met with in commerce in the shape of large irregular-shaped blocks, weighing on an average about 400 lbs. Externally this wood is deep brownred, but within, where no air has been in contact with it, its colour is brighter. It is very hard, and capable of taking a good polish; the blocks or billets are usually full of cracks and crevices; its taste is saccharine and astringent, and it colours the saliva red.

The Hamatoxylon campechianum is the tree which yields the wood in question. This tree also belongs to the natural order Leguminosae, and is a native of the entire warmer portion of South America, the larger American Antilles, viz., Jamaica, Cuba, St. Domingo, and also of Mexico. This wood has been known and used in Europe from a short period after the discovery of America, and since 1715 the tree has been cultivated in Jamaica. This wood has been the subject of an Act of Parliament, made in the twenty-third year of the reign of Queen Elizabeth, by which its use was forbidden as a dye-material, because it did not yield fast colours. This Act of Parliament was repealed, or at least superseded, by an order in council of Charles II., which sets forth that whereas great improvements had been made in dyeing generally, and greater skill applied especially as regards the means of obtaining faster colours from "black wood," the dyers might be allowed to use it, and Elizabeth's Act might remain in abeyance.

The following are the chief varieties of logwood, distinguished by names chiefly derived from the localities of exportation:—Spanish log, or campeachy wood, from Yucatan and Mexico; English logwood, from Jamaica; wood from St. Domingo; Honduras (British) wood; Martinique, and Guadeloupe or French wood; the last two kinds of less value as dye material than the others.

To the researches of Chevreul (1810) and to those of the late Dr. Erdmann, and of Runge of more recent date, we owe our knowledge of the properties and composition of the colouring matters of logwood. The colouring matter of logwood exists in the aqueous decoctions of that wood in three different forms:—In an oxidised state; as colourable matter, and is then known by, or designated as, hæmatoxylin; and, lastly, as a glucoside. The oxidised portion

is produced by the action of the atmospheric oxygen upon the wood, and it is to that alteration that the aqueous decoction owes its darkish tint. It is quite clear that this alteration may be more or less advanced, and, as a consequence thereof, common salt causes in concentrated liquid extracts (unless they have been made in vacuum) a precipitate of an almost black-coloured resinous substance, while in the freshly-made aqueous decoction the precipitate is of a bright brick-red. The colouring power of the wood is largely increased if it is suffered to ferment, after having been rendered moist, by being placed in heaps, on a well-made wooden floor, the height of the heaps attaining from I to I'5 metres: the wood thus heaped up should be frequently turned over, so as to renew the currents of air, and to prevent also a too great elevation of temperature. If "heating," as it is technically called, once sets in, it is not easily checked, and the colouring matter is soon entirely destroyed. This fermentation has the effect of partly eliminating and greatly modifying those substances which accompany hæmatoxylin: as a proof thereof we may state the fact that the so-fermented powder causes less soiling of the white portions of the cloth in the dyeing process. The increase of colouring power observed under these conditions is, in all likelihood, due to a saponification of the colouring glucosides.

Hæmatoxylin in a crystalline state was first obtained by Chevreul, by exhausting with alcohol the dry residue left on cautiously evaporating the aqueous extract of logwood. Prof. Erdmann prepared this substance by treating either the aqueous extract or the finely-pulverised wood, after previous admixture with pulverised quartz, with ether. The solution so obtained is evaporated to the consistence of a thick syrup, mixed with water, and, on being left standing by itself, the crystallised hæmatoxylin is deposited after some days. It now and then happens that, at the bottom of the casks or vessels wherein liquid extract of logwood is kept, brilliant crystalline tufts of hæmatoxylin are found in the shape of prismatic crystals, externally of a brownish metallic hue, but bright yellow within. The following are the properties of hæmatoxylin:-Bright yellow transparent crystals, yielding a yellowish-white powder, and belonging to the tetragonal system; in taste very like liquorice root; sparingly soluble in cold water, but far more readily so in alcohol, ether, and boiling water. The prismatic crystals contain 15'1 per cent of water. When a hot saturated solution of hæmatoxylin is left to cool in a stoppered bottle it deposits, after some time, granular irregular crystals, containing 5.6 per cent of water. Both these crystalline forms correspond to two different states of hydration.

According to Erdmann's analysis the formula of hæmatoxylin is $C_{16}H_{14}O_6$; the prismatic crystals contain 3 atoms of water, and the granular crystals only 1 atom. A portion of the water is expelled at 100°, but the last traces can only be volatilised at a higher temperature. When hæmatoxylin is heated it first fuses in its water of crystallisation; by continued and increased heat it is decomposed, leaving behind an abundant carbonaceous residue.

Hæmatoxylin is not volatile, and when quite pure acts as a weak acid, yielding with bases colourless compounds, which exhibit, however, a very great tendency to absorb oxygen and become coloured: we obtain, for instance, a precipitate which is at first white, but becomes rapidly bluish when exposed to air, and finally assumes a reddish-brown tinge. It is extremely difficult to

obtain a white combination of hæmatoxylin and the alkalies, because the affinity of that substance for oxygen is so greatly increased by the presence of potassa or soda, and it is, moreover, difficult to have hæmatoxylin in solution so completely free from any trace of oxidation, that the addition even of any alkali to a liquid containing it brings out at once a violet tint, which darkens rapidly on exposure to air.

A colourless alkaline hæmatoxylate may be obtained by taking advantage of the sparing solubility of these salts in a liquid containing common salt in solution. A cold decoction of logwood, or a solution of hæmatoxylin, is first saturated with common salt, and next a solution of caustic soda is gradually added; the first portion of the ensuing precipitate will be more or less coloured, because it carries down the oxidised substance, but by a rapidly managed filtration this portion of the precipitate may be eliminated, and on continued addition of alkali to the filtrate a white precipitate of hæmatoxylate of soda will be obtained, which becomes, however, rapidly coloured on access of air. Neutral and basic acetates of lead yield, with solutions of hæmatoxylin, bluish-white precipitates, which also become rapidly darkened by contact with air. Solutions of salts of gold and silver yield precipitates which soon alter, and deposit reduced metals; salts of copper also precipitate hæmatoxylin solutions. Protochloride of tin produces a permanent rose-coloured precipitate: solution of alum gives a bright red colour, but no precipitate is at first formed, though after some time a slight blackish-coloured precipitate ensues; acetate of alumina gives a fine purple. Dilute mineral acids have no particular action upon hæmatoxylin; concentrated nitric acid converts it into oxalic acid; chlorine converts it into a brown non-crystallisable substance, not thoroughly examined; chromic acid and bichromates are, in contact with hæmatin, instantaneously reduced, forming a deep black, which is extensively applied in cotton dyeing and printing.

The characters and reactions of the decoction of logwood, as first described by M. Chevreul, refer to mixtures of colourable matter (hæmatin) and actual colour (hæmatein). Dilute mineral acids turn the decoction yellow; if the acids are concentrated a red is produced. Since sulphuretted hydrogen enters, by causing deoxidation, into a colourless combination with the already more or less oxidised substances present, that gas or its aqueous solutions bleach the decoction. Sulphurous and carbonic acids turn the decoction yellow; alkalies produce first a red, and ultimately a violet; baryta, lime, and hydrated metallic oxides yield blue precipitates; basic salts act as bases, and acid salts like acids; aluminate of soda yields an abundant violet blue precipitate, insoluble in excess of alkali-this test is so delicate and so characteristic that by means of it logwood may be detected in a mixed decoction with great facility.* Hydrated protoxide of tin combines with the colouring matters of logwood decoction in the same manner as the alkalies, yielding a violet-lake. Protochloride of tin yields with the decoction a violet precipitate. Stannic hydrate acts as an acid, and turns logwood liquor red. Solution of alum vields first a yellow colouration, which after a while turns red. Salts of iron yield a blue-black (hence the application of logwood for the preparation of writing ink). Salts of copper give a blue precipitate. Salts of zinc yield a

^{*} E. Mathieu-Plessy, "Bulletin de la Société Industrielle de Mulhouse," vol. xxvii., p. 403.

deep purple precipitate; corrosive sublimate, an orange precipitate; chloride of antimony, a carmine precipitate; nitrate of bismuth, a beautiful violet precipitate.

When hæmatin is treated with caustic ammonia it gives a violet liquid, which, when heated to 100° in closed vessels for some time, becomes nearly colourless, owing to the reducing action of the ammonia. On cooling, this liquid becomes almost solid, from the precipitation of a white flocculent substance, soluble in acids, with a bright yellow colouration, and re-precipitable from that solution by alkalies, with a white colour. This substance, which contains the elements of hæmatoxylin and ammonia, acts as an organic base, and it becomes rapidly blue in contact with air. Dr. Schützenberger ascertained that this body contains nitrogen combined in another form—an ammoniacal salt.

When hæmatoxylin is heated to 140°, with anhydrous acetic acid, it yields a bright brown acetic derivative, insoluble in water, but soluble in alcohol. On evaporating the alcoholic solution the material exhibits an amorphous, resinoid, very fusible substance. Prof. Erdmann gave the name of hæmatein to the product of the action of hæmatoxylin when it absorbs oxygen in the presence of an alkali. When a saturated solution of hæmatoxylin in ammonia is gently heated, and shaken about so as to promote contact of air, the liquid assumes a deep cherry-red colour and deposits granular crystals of hæmateate of ammonia. When this is decomposed by acetic acid there is formed a bulky brown-red precipitate, which, on drying, becomes deep green and exhibits a metallic hue. When reduced to a powder this body is red. Hæmatein is sparingly soluble in cold water, but more readily at a boiling heat; it is soluble in alcohol, and slightly soluble in ether; its composition is expressed by C₁₆H₁₂O₆, differing from hæmatoxylin only by two atoms less hydrogen. Its formation is shown by the following formulæ:—

 $C_{16}H_{14}O_6 + O = C_{16}H_{12}O_6 + H_2O$.

Alkalies and ammonia dissolve hæmateine, yielding solutions which are at first blue or purple, but become gradually brown on contact with air and advancing oxidation. Hæmateate of ammonia is a deep violet powder, formed of very small microscopical four-sided prisms, which are transparent, soluble in water, with a purplish colour, and in alcohol with a red-brown: the hæmateate of ammonia loses its ammonia at 100°, or even in vacuo, over sulphuric acid. This salt precipitates solutions of metallic salts, giving rise to coloured precipitates, -- as, for instance, with sulphate of copper, a violetblue; protochloride of tin, violet; iron alum, a black precipitate; nitrate of silver is reduced to the state of metal. Hæmateine is therefore only the first term of the process of oxidation of hæmatoxylin. When the oxidation proceeds farther ulmic compounds are formed, as is the case with the alkaline solutions and under the influence of bichromate of potassa. Sulphuretted hydrogen decolourises hæmatein while combining with it, but does not reconvert it to hæmatoxylin; but probably the more energetic reducing action of hydriodic acid would effect the re-conversion.

The colourable substance of logwood acts as a phenol, capable of entering into combination with bases as well as with the radicals of the acids. In its general properties hæmatoxylin very much resembles bresiline, but they are not identical: it is probable, however, that hæmatin may be converted into bresiline by the addition of the phenyl radical.

For industrial purposes-that is to say, in dyeing-are used (1), the wood reduced to powder or shavings; (2), the cold infusion; (3), the decoction; (4), the extracts, in a more or less concentrated state, and sometimes even inspissated so as to form a dry material. The tinctorial value of these substances is estimated by a process of dyeing on the small scale precisely similar to that described for the Brazil woods; but since logwood is richer in colouring matter, only 5 grms. weight of that wood are taken for 25 square centimetres of tissue. The mode of manufacture of the extracts of logwood on the large scale will be afterwards separately treated. Logwood yields, with aluminous mordants, deep violet-grey shades; with proto-salts of iron a bluish-black, and with per-salts a black of a more brownish shade; a mixture of both yields a finer black than either separately. With chromates of potash logwood yields a black colour, which on exposure to light gradually takes a greenish shade. These colours are, however, unstable, and readily destroyed by the action of light, soap, alkalies, and acids. Logwood violet or logwood black is therefore very readily recognised by simply applying to the dyed fabric a drop of a somewhat concentrated acid, which has the effect of turning these colours red, while if the black be that of nut-galls the colour is changed, but not turned red. Logwood is very extensively used in the dyeing of cotton, wool, silk, leather, and in the preparation of some steam-colours: the tone of the colours varies according to the mode of application.

Logwood blue is produced upon cotton by working the goods in a beck containing a liquor or decoction of logwood, varying in specific gravity from 1.007 to 1.016, with the addition of acetate of copper. The liquid is raised from an ordinary atmospheric temperature to 50° in one hour. The blue thus produced resembles a vat-blue, and is very intense: this process of dyeing may be executed by alternately passing the woven fabric through a copper bath

and logwood bath.

In order to produce uniformly black-coloured grounds upon cotton, it is first mordanted with a suitable mixture of pyrolignite of iron and acetate of alumina, sometimes with the addition of nitrate of soda, to promote the oxidation of the iron. The dyeing operation is performed starting at 30°, and heating up to boiling; sumach or quercitron are occasionally added to the dye-beck. Uniformly black-dyed fabrics generally admit of being discharged if treated with oxalic acid. The printing of logwood colours upon cotton does not differ from the method just described herein, excepting that the aluminous or ferric mordant is printed on by the engraved roller instead of being uniformly padded. In order to fix the chrome logwood black, as it is termed, a mixture of a logwood liquor, properly thickened, is printed on, and, after drying, the fabric is placed in a bath of bichromate at 40°. The black colour thus produced is fast as compared with the other logwood blacks, and is the result of a special oxidation which hæmatoxylin undergoes under the influence of chromic acid: the lake thus produced contains oxide of chromium. Another kind of logwood black is obtained by printing a mixture of a logwood decoction to which protosulphate of iron and persulpho-nitrate have been added, and by passing the cloth so prepared through tepid milk of lime. By the aid of the bichromate process cotton-yarn or woven fabrics may be very cheaply dyed black: to 500 litres of the logwood extract, 1.007 sp. gr., are added 1.5 kilos. of bichromate of potassa, previously dissolved in water, to

which solution are added 3.5 kilos. of hydrochloric acid. The goods are placed in this mixture, and the temperature raised to boiling, when the fibre takes a deep indigo-blue, which passes into bluish-black after washing in water. The two last-mentioned dyeing processes resemble those in use for the fixation of catechu colours: there is, indeed, a similarity of behaviour, as far as the dyeing process is concerned, between hæmatoxylin and catechin. Uniform greys are obtained by means of logwood, by first mordanting the fabric by working in a weak solution of pyrolignite of iron. After oxidation and cleansing, the goods are dyed by being winced in a dye-beck containing the logwood reduced to powder, or in the shape of shavings, and by elevating the temperature gradually to boiling. The decoctions and extracts of logwood serve for the preparation of a very large number of steam and application colours, of the making up of which we quote the following as representing the ingredients:—

Steam-Black on Cotton.—Extract of logwood, at 6° Baumé (sp. gr. 1'044), 5 kilos.; acetic acid, 1'25 kilos.; pyrolignite of alumina, at 10° Baumé (sp. gr. 1'075), 1'25 kilos.; pyrolignite of iron, at 14° B. (sp. gr. 1'106), 1'25 kilos.; white starch, 750 grms. This mixture is to be boiled for an hour, and kept stirred until cold. It is next printed on, dried, and steamed.

Steam-Black for Roller-Printing.—Extract of logwood, at 17° B. (sp. gr. 1°134), 5°5 litres; pyroligneous acid, at 2° B. (sp. gr. 1°014), 2 litres; pyrolignite of iron, at 12° B. (sp. gr. 1°091), 6 litres; starch, 2°125 kilos.; gum substitute, 2°125 kilos.; oil, 0°12 litre.

Steam- and Application-Black for Roller-Printing.—Water, 2.5 litres; pyrolignite of iron, at 14° B. (sp. gr. 1.106), 11 litres; pyroligneous acid, at 2° (sp. gr. 1.007), 4.5 litres; extract of logwood, at 20° B. (sp. gr. 1.162), 6.75 litres; white starch, 3.508 kilos.; gum substitute, 4 kilos.; Gallipoli oil, 1.5 litres.

Bluish Application-Black.—Logwood decoction, at 4° B. (sp. gr. 1'029), 20 litres; white starch, from 3 to 4 kilos. This mixture is boiled, and after it has become cool there are added to it, of chlorate of potassa, 40 grms., and of rose-red liquor (mordant for), 2 kilos. The black produced by this mixture is very rapidly developed by exposing the fabrics in heated ageing-rooms.

Extract of logwood is also used mixed with the extracts of the red woods and of quercitron, for the production of brown and pomegranate application-colours upon cotton, while the logwood extract by itself is applied for steam-and application-lilacs. The following may serve as instances of the making up of these colours:—

Deep Lilac Colour for Block-Printing.—Water, 48 litres; extract of logwood, at 10° B. (sp. gr. 1.075), 8 litres; gum, 17 kilos.; alum, 3.8 kilos.; nitrate of copper solution, at 50° B. (sp. gr. 1.532), 250 grms.

Steam-Lilac for Roller-Printing.—Logwood extract, at 8° B. (sp. gr. 1.060), 8 litres; acetate of alumina, at 15° B. (sp. gr. 1.116), 1.5 litres. This acetate is made up of—Water, 5 litres; alum, 2.5 kilos.; acetate of lead, 1.8 kilos.; oxalic acid, 240 grms.; gum, 1.25 kilos.

Application-Lilac.—Logwood decoction, at 5° Baumé (sp. gr. 1°036), 10 litres; water, 4 litres; gum, 8 kilos.; sal-ammoniac, 750 grms.; salt for rose-red,*

^{*} Has been described above under Brazil Wood, and is prepared as follows:—12 kilos. nitric acid, at 30° B. (sp. gr. 1.261); water, 3.25 kilos.; sal-ammoniac, 1.25 kilos.; bichloride of tin, 2.5 kilos.; pure metallic tin, 1.5 kilos.

1.85 kilos.; sulphate of copper, 250 grms.; oxalic acid, 150 grms. In addition to the ingredients just named mordants are added, consisting of iron and alumina salts, or salts of tin: the addition of the salt of copper and of salammoniac is oxidising. Instead of the salt of copper the sulphuret of that metal may be employed, as proposed by M. Lauth.

Steam-Grey for Roller-Printing.—Water, 5 litres; pyroligneous acid, at 2° B. (sp. gr. 1'014), 0'5 litre; decoction of logwood, at 2° B. (sp. gr. 1'014), 1'5 th litre; quercitron decoction, of the same strength, 1'5 th litre; sal-ammoniac, 0'25 kilo.; gum substitute, 1'5 kilos. To every litre of this mixture are added 60 grms, of the undermentioned blue mordant, made up of—Ferrocyanide of potassium (yellow prussiate), 500 grms.; chlorate of potassa, 150 grms.; water, 0'75 litre; sulphuric acid, at 65° B. (sp. gr. 1'827), 640 grms., diluted with 0'12 litre of water: the acid and water should be mixed and left to cool before being added to the rest of the ingredients.

These steam-greys may be varied in divers ways; for instance—Logwood decoction at 2° B. (sp. gr. 1·014), 2·5 litres; pyroligneous acid, at 2° B. (sp. gr. 1·014), 1 litre; red liquor (mordant as used for madder colours), at 8° B. (sp. gr. 1·060), 2·5 litres; water, 13 litres; pyrolignite of iron, at 10° B. (sp. gr. 1·075), 2·5 litres; starch, 2·25 kilos.

Application-Grey.—Water, I litre. The following substances should be dissolved therein or added thereto:—Gommeline, I kilo.; solution of gum tragacanth, 0·125 kilo.; pyroligneous acid, at 3° B. (sp. gr. I·022), 0·060 litre; solution of sulphate of iron, at 20° B. (sp. gr. I·162), 0·18 litre [such a solution contains about 28 per cent of the crystallised salt]; red liquor, as used for madder, 0·060 litre.

Logwood decoctions also enter into the preparation of olive, reseda, oakbrown, and some other dyes. In dyeing wool and silk with logwood, blue is obtained on wool by mordanting it with alum and cream of tartar, and immersing the woollen material in a boiling bath of logwood, or extract thereof, to which sulphate of copper has been added,

For the so-called king's blue the following quantities are used:—For too kilos. of wool: alum, 10 kilos.; cream of tartar, 2 kilos.; sulphate of copper, 1 kilo.; shavings of logwood, a sufficient quantity.

Logwood is also employed for the production of French blue upon wool, along with indigo, santal, orchil, and nut-galls.

The well-known excellent Elbeuf and Sedan blacks, on broad cloth, are dyed first more or less deep blue, by means of the indigo vat, and afterwards dyed black, in a boiling bath made up of logwood, sumach, and sulphate of iron. If the cloth is not first indigo vatted, it is mordanted with alum and red argol, and dyed in a bath to which logwood, fustic, orchil, alum, argol, and copperas are added.

A fast black upon wool, which does not fade, is produced with logwood, when the woollen fabric is first mordanted with bichromate of potash and cream of tartar, and next dyed with logwood, orchil, and alum. On the Continent the best blacks upon woollen tissues of superior description are very generally obtained by means of madder.

The fastest logwood-black upon woollen and worsted goods is that obtained by the old logwood and copperas process. It is now little used, not from any imperfection in the results, but because it requires more time, labour, and space than the modern chrome-blacks. These are rapidly completed, and look well for a time, but on prolonged exposure to direct sunlight they assume an unpleasant greenish hue. A logwood and copperas black upon a vatted—or, as it is technically termed, woaded—bottom yields in permanence only to a madder-black upon the same ground. It is not inappropriate to remark that dyers have much less inducement to study fastness than was formerly the case, as the rapid changes of fashion leave consumers no time to discover the fugitive character of the shades.

By adding, to the logwood or its decoction, fustic, * santal wood, turmeric, and alum, there are produced upon woollen fabrics, previously mordanted with bichromate and cream of tartar, beautiful bronze colours, of various shades. The dyeing operation is carried on at boiling heat.

Steam-blacks for wool are made up of—Extract of logwood; a salt of copper (sulphate, chromate) as oxidising material; alum as mordant; pernitrate of iron as mordant, and oxalic acid; sometimes bichromate of potassa and sal-ammoniac are also added.

Steam-grey for wool contains—Extract of logwood; nitro-sulphate of iron. Logwood is also employed for some kinds of steam-brown and fancy colours on wool.

Steam-black upon silk is produced by printing a properly thickened mixture of logwood decoction, extract of nut-galls, a salt of copper, generally the nitrate, and a proto-persalt of iron. Silk is dyed black by means of logwood, or the decoction thereof, after having been mordanted in either sulphate of iron (proto-salt), or in a mixture of that salt and nitro-sulphate of iron, or also in nitrate of protoxide of iron. Silk is very frequently dyed black by a twice or thrice times repeated immersion in the dye-beck, and the colour is modified, if required, by the addition of fustic. If the proto-nitrate of iron is used as a mordant for silk, that material, after dyeing, becomes very harsh, and its suppleness and pliancy is therefore restored by padding in emulsified olive oil. The brilliancy of black silk is often enhanced, and its weight very considerably increased, by immersion in a solution of subacetate of lead, and exposure to an atmosphere of sulphuretted hydrogen gas.

Logwood dyes are detected on dyed fabrics by the following tests:—Logwood-black dyed tissues leave, on incineration, ash composed of peroxide of iron, or a mixture of that oxide and alumina, or also, sometimes, of oxide of chromium. The dyed tissues are discharged by chlorine and hypochlorites, and are turned red by hydrochloric acid and tin-salt: when the reddened spot, while yet moist, is pressed against white filtering-paper, it yields thereon a cherry-réd stain, which turns blue if touched with a glass rod moistened with aluminate of soda.

The lilacs or violets produced by logwood leave, on incineration, a white ash containing alumina: the dyed tissues are discharged by chlorine and hypochlorites, and turn red with hydrochloric acid, presenting, further, the same features as those just described for black. When the lilac or violet goods are put into milk of lime, and next washed with soap, the colour is discharged.

^{*} Of this we shall say more hereafter, but it may be briefly stated to be the wood of the Morus tinctoria. It is known in the trade also as Cuba wood, and largely used, especially in woollen dyeing.

RED COLOURING MATTERS.

Cochineal, Kermes, Lac-lake, Gum-lac, Lac-dye.

The beautifully red substance known in commerce as cochineal is the dried body of an insect belonging to the order Homoptera and family of Coccidæ. Although the discovery of the coal-tar colours has greatly diminished its consumption as a dye-ware, it is yet largely used for the production of crimson and scarlet on wool and worsted. The red dye insects inhabit various plants, and are distinguished as: - Genuine cochineal or Coccus cacti; Coccus ilicis or kermes; Coccus lacca or Ficus; Coccus cerificus and Coccus polonicus radicens. The family Coccus is divided into two groups, the one including the insects not yielding any colour at all, while the other contains pigment, and these are especially termed cochineal. These insects are not larger than a small pea or lentil, and live upon those parts of certain plants which are exposed to air or on the roots. The insects exhibit the shape of an oval shield, it being difficult to distinguish their head, thorax, and abdomen with the naked eye. As a rule the females remain fixed to those parts of the plants to which they fasten themselves with their suckers. The male insects, however, move about, and sometimes are even provided with wings so as to be able to fly, but they are only few in number, and do not make their appearance until an advanced period of the season. The females remain stationary after having laid eggs; and, dying soon after, their dried-up shell or shield serves as a shelter for the eggs, whence has arisen the erroneous notion that they are vivipara. The natural term of life of the insects is about a year; when fully developed they appear as small hemispheres fixed by the base upon the surface of the plant; sometimes the shape is more ovoid; their colour varies from brown to red, or from violet to black.

The insect known as cochineal lives upon a species of cactus (the Cactus opuntia or Nopal, or also Opuntia coccinilifera), a plant which grows in a wild state in Mexico, but which for the sake of the insect alluded to is cultivated in gardens, being termed nopaleries. The flowers of this plant are small; the colour is red or yellow. The whole of the Cactaceæ seem to be rich in red colouring matter, whence has arisen the question whether the insect really originates the red colouring matter, or only collects and elaborates what is pre-existent in the plant. In Mexico and Central America two kinds of cochineal are distinguished, viz., the Mestèque, or grana fina, home-grown or fine cochineal, principally grown in the Mexican Province of Mestèque and in Honduras, and the wild or forest cochineal, grana silvestra, collected from the wild nopal. The former of these is more valuable than the latter, because it is far richer in colouring matter. The Mexican Indians cultivate the nopal plant sometimes in gardens near their dwelling houses, sometimes, also, at more remote places towards the forests, where a spot is cleared by burning the trees and properly tilling the soil so as to render it fit for the culture of the cactus, which is reproduced from the shoots, and is fit for receiving and feeding the insects after a lapse of two years.

The harvesting of the insects takes place before the setting in of the rainy season, while the reproduction of the insect is secured by cutting off from the nopal plant such young twigs as are covered with the young brood. These are placed under shelter from the stormy weather, and kept until the return of

the fine season, when the insects are brought to the nopal plantations again, placed in moss. This operation takes place in the plains during the month of August, and during November on the table-lands. A moderately warm climate is best suited for the insects, which soon after having been placed in the plantations deposit their young brood by thousands in the shape of granules the size of small pins' heads. The young spread over the nopal plant, and fix themselves thereon with their suckers. After the lapse of some three or four months a first gathering of the Coccus takes place, just before the females begin to deposit their eggs, and when a few young insects are to be seen on the plants; the insects are gathered either in baskets made of straw, or, better, in basins of tinned iron, and provided with a contrivance suitable for embracing or enclosing the articulations of the plant, while the . insects are removed from the leaves by means of a soft brush. A number of females are left on each plant for breeding purposes, and thus a new generation is produced, which is again gathered before the rainy season sets in. This second gathering is effected by means of scraping off from the surface of the leaves of the cactus the insects with a blunt knife; the effect is, that not only the full grown, but also only half developed insects are removed, and a product obtained which, under the name of granilla, is less esteemed in commerce. The insects are killed by being immersed in boiling water for a moment, and are next dried either in the sun or in ovens expressly arranged for this purpose. By this treatment the peculiar white down which covers the insect is lost, and its red-brown colour becomes apparent. Such kind of cochineal is known as Renegrida. Very frequently the insects are enclosed in a linen bag and killed by being placed in an oven. In this case the natural grey colour is preserved, and the cochineal thus treated is known as Jaspeada. The best mode of killing the insects is to expose them for a few moments to the vapours of boiling water. In Mexico the insects are dried on the iron plates used for baking maize cakes, an operation which imparts to the insects a blackish colour, and hence it is known as Negra. The female insects which die after having laid their eggs lose more weight on drying than the females which are killed while with young. 4 kilos. of the first kind and 3 kilos. of the latter kind yield I kilo. of dry cochineal. I hectare (2.471 English acre) produces about 300 kilos. of cochineal with the labour of three men; 140,000 insects produce I kilo. of dry cochineal.

Dried cochineal exhibits an orbicular shape; its colour is blackish, reddish, or grey; its diameter varies from 2.05 to 3 millimetres. If a few grains are steeped in tepid water they swell up, assume an hemispherical shape, while then, also, the peculiar form of the insect becomes distinguishable, so that the body, head, the articulations where the feet are inserted, and the sucker are readily visible. When the insect thus swollen up is pressed it bursts, emitting thousands of very small deep red-coloured granules, presenting the appearance of eggs, but viewed under the microscope these granules are recognised as fully developed young brood. The Mestèque cochineal is white, covered by a mealy powder, while the wild cochineal is smaller sized and enveloped with a downy wool-like substance, which prevents the articulations and shape of the insect from being seen. Notwithstanding all these facts, which prove the animal nature of cochineal, it was for a long time considered of vegetable origin.

In the year 1502, Lopez de Gomara, and, exactly a century later, Plumier,

stated that cochineal was an insect; they even described it carefully, and also the plant on which it lived. The Dutch physician and naturalist, Hartsoeker, called attention to this subject in 1694, and so did De la Hire in 1704 and Geoffroy in 1714; but no one would believe their statements, and it was not until 1729 that, through the assiduous researches of Dr. Ruisch, who went on purpose to Mexico, where he visited the nopaleries of Oaxaca, and published a work on this subject,* that the question was settled. Mexico has for a length of time been the chief cochineal-producing country, it being obtained from the provinces of Tlascala and Oaxaca, as also from Guatemala and Honduras, in Central America. Oaxaca alone used to yield annually some 400 serons. Spanish vessels used to import into Amsterdam about from 2000 to 3000 serons of cochineal annually, each seron containing from 130 to 200 lbs. weight.

The cultivation of cochineal was practised in Mexico by the Aztecs long before the conquest of the country by the Spaniards. The old Spanish Government of Mexico caused the nopal plantations in Yucatan to be burnt, in order to enhance the price of cochineal. It is only since 1830 that the cultivation of the nopal cactus and the cochineal insects has been spread into Spain, near Malaga and Valencia, the Canary Islands, Algeria, and Java. All these plantations have succeeded, but the most productive are those of Java. Professor Girardin gives the following account of the different commercial kinds of cochineal:—

1. Honduras cochineal is brought directly to England; it is a very superior quality of cochineal, and is classified as—(a) Black or zacatilla, blackish or brownish red, shiny, and bearing the traces of a whitish-coloured envelope; the powder of this species is carmine-red coloured, but in water it becomes deep red-brown. The value of this substance is about 19s. the kilo. (b) Grey or silvery-coloured cochineal; wrapped up in a whitish mother-of-pearl-like but pulverulent coating, consisting of a peculiar volatile substance, which seen with a magnifying glass exhibits a very distinct crystalline appearance. In the state of powder its colour is less deep than that of the foregoing, and the colour of the moistened powder is less intense. The value of this kind is about 17s. a kilo. (c) Reddish cochineal, only covered with a white powder in the wrinkles of the body. This kind is less valuable, and does not fetch more than about 15s. the kilo. All these qualities are imported either in sacks covered by basket work made of cane, or in bags made of leather, and then termed serons, each package weighing from 75 to 80 kilos.

2. Vera-Cruz cochineal, so named from the port of exportation. This is chiefly sent to Bordeaux or Havre in serons weighing from 80 to 100 kilos. The first quality is known as zacatilla; the second as grey; the third as reddish. The insect should be hollow, light, and much shrunk. The sort which is coarse grained, dull looking, mixed with small and resinous particles, is the least valuable.

3. Cochineal from the Canary Islands is imported into Cadiz or Marseille. It is not met with at all in large quantity, but the quality is superior even to that from Mexico. It is packed either in small sacks weighing from 25 to 30 kilos., or in small boxes or casks.

^{* &}quot;Histoire Naturelle de la Cochenille," Amsterdam, 1729, in 8vo., p. 175; also "Philosophical Transactions," xxxvi., p. 265.

4. Java cochineal is imported into Amsterdam and Rotterdam direct by the Netherlands Society for Trade. It is packed in small tinned iron boxes (square canisters), placed inside stout wooden cases, and varying in weight from 40 to 60 kilos. This cochineal is reddish coloured; its tinctorial value is below that of the zacatilla kinds, but better than the wild cochineal. The quantity annually brought to Europe is considerable, and it is owing to the cultivation in Java that the price of this article has greatly fallen.*

Animal or Vegetable Kermes, Scarlet Grain, Oak Cochineal (Coccus ilicis).—The oak kermes or green oak with prickly leaves (Quercus coccifera) is a tree which is found in large numbers in the South of France, Spain, Italy, the Greek Islands, and in Candia. The kermes, an insect living upon the leaves of this tree, is gathered by the peasantry, and is so little known at present in England that when occasionally (yet rarely, and at great intervals of time) a parcel of this substance arrives in London hardly any of the brokers recognise it. It is more extensively used in France. No colouring substance or other material used in dyeing possesses so great an antiquity; it was known in the time of Moses, and is mentioned by its Hebrew name Tola. Its name, Coccus, frequently occurs in the Greek and Latin writers. Kermes, like cochineal, was supposed to be berries or grains, and colours dyed with them were said to be grained or engrained, and since the kermes colours were fast and durable the term grained expanded in its signification, and meant a fast colour whether dyed with kermes or not. But kermes are insects, and the word is Arabic, signifying "little worm," and in the middle ages they were called Vermiculi, and the cloth dyed with them Vermiculata, whence through the French we have vermillion, a word now employed as the name for one of the compounds of sulphur and mercury. The term crimson is also derived from kermes through the Italian and French languages. Kermes when alive on the trees is fixed to the twigs either in groups or alone. It appears as if forming bluish berries, covered with a whitish powder; it occurs in commerce as pale reddish brown grains, which colouration is due to the vinegar used for killing them. Kermes may now be considered as having merely a historical interest, and need not, therefore, further occupy our attention.

Gum-lac or Resin-lac .- The substance known as gum- or stick-lac is a product of India, which, when having undergone some preparations, is known as lac-dye, lac-lake, or simply lac. It is derived from the Coccus lacca or Ficus, an insect which lives on the young twigs of various kinds of trees, more especially the Ficus religiosa and Indica, the Rhamnus jujuba, and others. The unprepared material, stick-lac, is a kind of resinous crust adhering to the twigs, and is the product of the digestive organs of a smallsized insect, no bigger than a pin's head; its body is oval shaped, somewhat flattened, and composed of twelve red-coloured rings; its antennæ are half as long as its body, which is at its posterior part provided with two divergent hairs. These insects appear in November and December, when they walk about for a short time on the twigs, and in January they fasten themselves to the fleshy succulent portions of the young branches. Gradually the

^{*} Girardin, "Traité de Chimie Appliquée," vol. ii., p. 553. Persoz, "Impression des Tissus," vol. i., p. 509. Thiery de Menonville, "Traité de la Culture du Nopal, et de l'Education de la Cochenille," 2 vols. in 8vo., Paris. 1787.

abdomen of the insects becomes surrounded by a viscous transparent liquid, which glues them to the plant, and which, continuing to be secreted, forms a cellule surrounding the animal. The substance composing this cellule is the stick-lac. The cellule attains its full size in March, and the insect then exhibits the appearance of a red oval-shaped, smoothly-polished, lifeless sack, entirely filled with a beautifully red liquid; its size is then about the same as the full-grown cochineal. So it remains for some months, until in October the liquid will be found to contain twenty to thirty young insects. The old inhabitant of the cell dies, and the young brood leave the cell by piercing the top. The stick-lac when carefully viewed will be seen to contain the pierced, empty, somewhat hollow cells. The young brood is so closely packed together that out of a number of six only one finds room to construct its cells by being enabled to pierce the twigs of the trees; the remaining insects die or are devoured by birds. The young twigs of the trees, which are inhabited by the insects, appear as if dusted over with a red powder, and the presence of the insect causes the death of the twigs by exhaustion. The insects are carried from one tree to another by the feet of birds.

When an incision is made in the softer branches of any of the trees upon which this insect lives, a milky juice exudes, which coagulates instantaneously, yielding a glutinous material, which after drying resembles stick-lac. The stick-lac of commerce is chiefly gathered along the hilly banks of the Ganges, and in sufficient quantity to supply all demands. The stick-lac best suited for dyeing purposes should exhibit a deep red colour; the pale-coloured perforated kind is only fit for varnish-making, because it does not contain the insects. The stick-lac covers the branches of the trees to a thickness of some millimetres, the cellules being placed longitudinally. Their diameter is 5 millimetres, and each contains the carcase of a dead insect. The resin obtained from this material is amber-coloured, and is known as shellac. We do not know whether the lac is secreted by the animal after it has been modified by passing through its organs, or whether it is directly produced from the vegetable parenchyma of the tree by the piercing of its bark by the insect.

In India the lac, that is to say the resin, is applied by the natives for various ornamental purposes, viz., the making of bracelets, neck-chains, and the like; also as sealing-wax, and for preparing varnish. In Europe it is used for dyeing and varnish.

She'lac, the main constituent of our sealing-wax, is, as already noticed, produced by the insect, but the shape it is met with in trade is due to artificial preparation.* The tree known as Celastrus ceriferus, a native of India and the warmer part of China, and producing a wax largely used in these countries for candle-making, supports an insect of the same kind known as Coccus ceriferus. The Chinese cultivate this insect, and it yields a waxy red-coloured substance, known as pela.† Of stick-lac the following varieties occur:—

r. Stick-lac in sticks gathered in March and October. The cellules are fastened to the twigs upon which they were formed. It is a hard, dark red, transparent resin, which shines when broken; if chewed it colours the saliva

t "Anderson, "Monographia Cocci Ceriferi," 1791. Pearson, in "Phil. Transactions, 1794, p. 383.

^{*} Kerr, "Phil. Transactions," lxxi., 1781, p. 374, Figs. 1 to 6. Kerr, "Roxburgh Transactions," lxxxi., p. 228. "Asiatic Researches," ii., 1799, p. 361. Virey, "Journal Complém du Dict. des Sc. Méd.," x., 1821, 193, Figs. 1 to 7.

violet, its taste being astringent and bitter. It is insoluble in water, to which it, however, imparts its colouring matter, rendering it red. It is partly soluble in alcohol, yielding a red solution, but it is insoluble in fatty and essential oils. Its composition is, according to Hatchett—Resin, 68; colouring matter, 10; wax, 6; gluten, 5.5; foreign matters, 10.5. Dilute sulphuric and hydrochloric acids are better solvents for the colouring matter than water, whence they are applied in the lac-dyeing process. The best kind of this variety of stick-lac is imported from Siam, the Bengal product being very inferior.

2. Grained lac consists of the cells detached from the wood of the branches. It occurs in small, variously-shaped, broken-up pieces, and, as met with in trade, is frequently robbed of a portion of its colouring matter by treatment with water. It consists of—Resin, 88.5; colour, 2.5; wax, 4.5; gluten, 2.0; woody fibre, sand, &c., 2.

3. Lac in the shape of cakes is simply the material just mentioned after having been fused and cast into moulds.

4. Lac in the shape of thin scales is obtained in the following manner:—
The crusty resinous substance is pulled from the branches of the trees, broken into small fragments, macerated for twenty-four hours in cold water, washed, dried, and put into a bag made of stout calico, which is tied at the mouth, and placed over a clear charcoal fire. The resin liquefies, and on pressure being applied the molten material runs in thin layers over a plank of polished fig-tree wood, when it soon solidifies. This material goes by the name of shellac, and contains 91 per cent of resin, only about ½ per cent of colouring matter, while the rest is wax, gum, and other substances.

Lac-lake and lac-dye are the secondary- or by-products of the process just described, carried on with the following modification:—The crude matter as taken from the trees is coarsely powdered and exhausted by maceration in hot water, to which sometimes a little soda is added. The liquid thus obtained, sometimes after previous filtration through coarse canvas, is evaporated in pans placed on a charcoal fire, or left to spontaneous evaporation by the sun's rays in shallow earthenware vessels. The dry residue is in the shape of square cakes, 36 millimetres by 13. This material consists on an average of-Resin, 25; colouring matter, 50; earthy impurities, 22. It is shipped from Calcutta, and is chiefly brought to London and Hamburg. This substance has been known and prepared in India for centuries; its English name was given to it by Mr. Stephens, who at the end of the last century made it known in Europe.

Although the colouring matter of lac-dye is analogous to that of cochineal, its identity is not established, the shades produced being less bright but more permanent. The richness of this and similar products in colouring matter is determined in the same manner as has been stated for cochineal, viz., by a dyeing process on the small scale. The lac-lake is obtained by precipitating with alum the decoction of stick-lac prepared with weak caustic soda. The ensuing deposit is pressed, moulded into cakes, and dried. It consists of—Colouring matter, 50; resin, 40; alumina, 9; impurities, 1. For dyeing it is best first decomposed by weak hydrochloric or sulphuric acids. There are met with in commerce a great number of brands of lac-lake and lac-dye, but the trade-mark is no guarantee of the quality.

Messrs. Brooke, Simpson, and Spiller have introduced into commerce a lac-dye superior to that imported from India. Their improvement consists in treating stick-lac with weak ammonia, and adding to this solution chloride of tin, when a fine red insoluble matter is formed, and precipitates. This is collected, and is ready for use. These different preparations are chiefly applied for dyeing woollen fabrics scarlet; 2 to 3 parts produce the same effect as 1 part of cochineal. In order to neutralise the influence of the alumina, a larger proportion of tin solution is required to be added to the acidified dyeliquor.

The India Museum (India Office, Westminster), contains a very complete and valuable collection of all the substances here described, and also of various products which are never met with in the European trade, belonging to this class of materials.

What is, or at least was, known as Polish grain, Coccus polonicus, or Polish kermes, is an insect living on the roots of the Scleranthus, a plant growing wild, in various parts of Central Europe, in a sandy soil. This insect—of the size of a peppercorn, exhibiting a purplish-red colour—was formerly gathered about the middle of June, but now it is altogether forgotten, having been displaced by cochineal.

As far as the colouring matters of genuine cochineal and stick-lac have been investigated, it appears that, if not identical, they at least agree closely in their properties. Cochineal owes its tinctorial properties to a red acid, soluble in water. Within the body of the living insect the colouring matter is present, not in the state of solution, but as small granules grouped around a larger colourless nucleus, in state of suspension, in the midst of a colourless liquid. The insect is richest in this substance just before the period of laying eggs. This acid, though in an impure state, was first isolated by MM. Pelletier and Caventon, who called it carmine, considered it to be a nitrogenous matter, and expressed its formula by C₈H₁₃NO₅. Arppe, Warren de la Rue, and Hugo Müller proved it to be an acid, and found that in a perfectly pure state it does not contain any nitrogen, though it is accompanied by nitrogenous matters, which render its purification very difficult. According to the authors just named, the pure substance in the amorphous state consists of C14H14O8. Carminic acid in crystals, as obtained by Dr. Schützenberger, consists of CoH8O5; but Dr. Schaller, who also obtained this acid in a crystalline state, represents this composition as CoH8O6. Dr. Schützenberger found, moreover, that the colouring matter exists in cochineal in two degrees of oxidation; to one of these the formula CoH8O5 belongs, and to the other CoH8O7, Schaller's formula being intermediate. Schützenberger, however, desires that these researches should be taken up by some one, in order to settle this point definitively.

Carminic acid may be obtained readily in the crystalline state by the following process:—Cochineal is exhausted first with ether, which removes fatty matters, and next with boiling water. The red liquid is precipitated with neutral acetate of lead, slightly acidified with acetic acid. The bluish-violet precipitate which falls carries down all the colouring matter, and the filtrate is nearly colourless. When well washed with hot water the precipitate consists chiefly of carminate and phosphate of lead, mixed with a small quantity of nitrogenous matter, a larger portion of which is found in the filtrate, which, on

being evaporated to a syrup, yields tyrosine in crystals. The plumbic precipitate is suspended in water, and decomposed by sulphuric acid, taken in sufficient quantity to effect the conversion of the whole of the lead-salts present into sulphate. The liquid is filtered while hot, and the carminic acid thus set free is dissolved in the filtrate, while the phosphoric acid remains with the residue upon the filter. The filtrate is evaporated to dryness, at 50°, on a water-bath, and the dry residue is taken up by absolute alcohol. When the partly evaporated alcoholic solution is cooled, the carminic acid is obtained in a crystallised state, exhibiting a somewhat red, cauliflower-like, appearance. The crystallised mass contains frequently, however, yellow hexagonal-shaped crystals, which may be separated by treatment with cold water, wherein these crystals are insoluble. The filtrate, again evaporated, is either again taken up by absolute alcohol or by ether, because, although the carminic acid is sparingly soluble in that liquid, it yet yields the cauliflower-like shaped mass. Pelletier and Caventon prepared their carmine (an impure carminic acid) by exhausting the cochineal, previously treated with ether, with boiling alcohol. This solution, when concentrated, yielded a semi-crystalline precipitate, which, when again dissolved in alcohol, gave, on the addition of its own bulk of ether, a precipitate of carmine. The product thus obtained appears to be a compound of carminic acid and a nitrogenous substance (tyrosine?)

Pure carminic acid is a solid, purplish-red substance, which, when reduced to a very finely-divided powder, is bright red; it crystallises, as already observed, from its alcoholic solution, tastes decidedly acid, is very soluble in water and alcohol, but hardly soluble in ether. It may be heated to 136° without decomposition. It dissolves, without decomposition, in strong sulphuric and hydrochloric acids; the haloids readily and rapidly destroy it. Nitric acid of sp. gr. 1.4 converts it into oxalic and nitrococcussic acid, while red vapours are given off. Nitrococcussic acid is a nitrated compound, forming yellow-coloured foliated crystals, of the formula C₈H₅(NO₂)₃O₃+H₂O. The aqueous solution of pure carminic acid is not spoiled by contact with air; caustic alkalies colour it purplish-blue; with lime and baryta water purplishblue precipitates are thrown down; the acetates of lead, zinc, copper, and silver yield purplish precipitates. The argentic precipitate is readily decomposed, metallic silver being set free. Alum does not cause a precipitate in this aqueous solution unless some ammonia be next added, when a carmine lake is thrown down. Hydrate of alumina immediately withdraws carminic acid from its solutions; the ensuing compound remains red as long as heat is not applied, but if heated becomes first carmine-red and next violet. The same effect is produced by the addition of a drop of any acid, or a small quantity of any solution of a salt of alumina, while alkalies, on the other hand, give stability to the red colour. The neutral alkaline salts turn carminic acid to violet, while the acid salts of alkalies (bitartrate of potassa, for instance) render the shade more orange. Neutral salts of lime, baryta, and strontia give a violet colouration to the aqueous solution; sulphate of lime produces a precipitate.

The chemical history of the carminates is as yet very far from complete. The alkaline carminates are soluble; the others are, as far as ascertained, amorphous, pulverulent substances. Carminate of soda, in the shape of purplish-coloured foliated crystals, may be obtained by cautiously adding

alcohol to an aqueous solution of that salt. According to Schaller, carminate of soda may be obtained in crystals from its aqueous solution; its formula is $\frac{C_9H_8O_4}{Na_2}$ O_2 . Nascent hydrogen reduces solutions of carminic acid, but the red colour returns on contact with air.

The decoctions of cochineal behave, to some extent, differently with reagents, this difference being due to the presence of nitrogenous substances and phosphates. The following are the characteristic reactions of a decoction of cochineal: -Acids turn the colour to a vellowish-red, the fieriest shade being produced by oxalic acid, and cause a slight precipitate; alkalies turn the colour violet; lime-water gives a violet-coloured precipitate; alum turns the colour first red, and then gives a precipitate; chloride of aluminium, reddish-violet precipitate, the supernatant liquid being amaranth-coloured; chloride of tin turns the colour yellowish, forming a cherry-red precipitate; chloride of tin (as usually met with in the trade), violet precipitate; bichloride of tin turns the colour to scarlet; sulphate of iron gives first a violet-grey, and next a precipitate; acetate of iron, a brown-coloured precipitate, turning to olive; sulphate of copper and lead salts, violet-coloured precipitates; proto-nitrate of mercury, a precipitate exhibiting the colour of dregs of wine; per-nitrate of mercury, a brownish-red precipitate; sulphate of zinc, deep violet precipitate; cream of tartar, salt of sorrel, and alum, yield each red precipitates, constituting the carmine of commerce.

Ammoniacal Cochineal.—When a solution of carminic acid in ammonia is for some time left to itself a modification takes place, whereby the acid combines intimately with the elements of ammonia, there being formed an amide or an amidated acid: this fact, long since known, has been utilised for the preparation of a new colouring matter, termed ammoniacal cochineal, or carminamide. This colouring matter does not produce red and scarlet colours, but violets, amaranths, and mauves, and the action even of oxalic acid in excess does not turn the colour of this pigment to yellowish-red. With bichloride of tin a deep violet, not a scarlet, precipitate is formed. There are met with in commerce two different kinds of ammoniacal cochineal, in cakes and in paste; the former is prepared by digesting for three months, in a closed vessel, 3 parts of ammonia and 1 part of ground cochineal. The liquor is decanted, and then is added to four-tenths of its weight of gelatinous alumina. This magma is evaporated in a copper basin, so as to expel all ammoniacal smell, when the thickish mass is cut up into the shape of cakes, and dried. The paste is prepared in a similar manner, but the operation only lasts eight days; the liquor is evaporated to two-thirds of its bulk, and no alumina is added: this paste is one-third less rich in colouring matter. Dr. Schützenberger states that the colouring matter of the ammoniacal cochineal of commerce, and also that obtained by the direct action of ammonia upon carminic acid, contains nitrogen in another form than that of an ammoniacal salt; and the formula of this compound is C₉H₉NO₄.

The substance known as carmine is a preparation of cochineal, exhibiting a very bright red colour; it is met with in commerce as an almost impalpable powder, or as cakes packed in thin glazed paper or in small boxes; it is also sold mixed up with white of egg, gelatin, or isinglass solution: the value of this substance depends upon various causes, but its beauty and the fineness of

powder are the chief points which determine its price, and the purer the material the better are its qualities.

Pure carmine is entirely soluble in ammonia, and upon that property its use in the dyeing of tissues is based. The true nature of the combination of carminic acid which forms this compound is unknown; in its formation the intervention of the nitrogenised matters naturally present in cochineal, or of those which can be added to a solution of carminic acid, is required. The preparation of carmine itself is not a matter which is very well known; every maker keeps secret that method which yields him the most beautiful and remunerative product. According to Prof. Girardin, the manufacture was accidentally discovered, at Pisa, by a Franciscan monk, who, while experimenting with cochineal and carbonate of potassa, observed, on adding an acid to that mixture, the precipitation of a beautifully red-coloured substance. Dr. Homberg published, in 1656, a method for the preparation of carmine. Generally speaking carmine is prepared by exhausting previously pulverised cochineal with boiling water, to which sometimes an alkaline salt is added; and the precipitation of carmine is effected either by a weak acid or an acid salt. Sometimes albumen or gelatin is added to the liquid, and also alum.

The following prescriptions are practical, and give an idea of the method of preparation of this colouring matter:—Take ½ kilo. of powdered cochineal, boil with 10 litres of water for a quarter of an hour, add 30 grms. of alum, boil up for three minutes, let settle; the clear liquid carefully decanted will deposit, on standing for a few days, from 40 to 50 grms. of carmine; the clear decanted liquid deposits, after some few days longer rest, another but smaller quantity of carmine of inferior shade. Or, take 1 lb. of powdered cochineal, 30 lbs. of water, boil for a quarter of an hour, add 30 grms. of best cream of tartar, boil for ten minutes longer, then add 15 grms. of alum, and boil up for a couple of minutes; the clear and decanted liquid is left to deposit in shallow glass vessels; the carmine is washed with cold distilled water, and dried carefully in the shade.

The following is the prescription of Madame Cenette, a lady once in very extensive business in carmine making):—Take 2 lbs. of ground cochineal and 150 lbs. of water, boil for two hours; add 3 ozs. of pure nitrate of potassa, boil for three minutes longer; add next 4 ozs. of salt of sorrel, boil again for ten minutes; after the liquid has become clear, by standing for a quarter of an hour, it is set aside in shallow glass vessels for three weeks, after which time the carmine which has deposited is carefully separated from the liquid, which, meanwhile, has grown mouldy on the top; the carmine is dried in the shade.

The carmine of commerce is often adulterated with starch, kaolin, French chalk, vermillion, and sometimes contains small bits of cochineal. Since pure carmine is readily and entirely soluble in ammonia, such adulterations are readily detected.

Carmine is chiefly used by artists in oil and water colours, for the colouring of superior bonbons, artificial flowers, and, in rare cases, the printing of tissues. Carmine is chiefly made in Germany, whence it is exported into other countries. France obtains annually about 400 kilos. of superior, and 3500 kilos. of common, carmine from Germany. Carmine of the highest quality, it should be here observed, can only be prepared under certain peculiar

conditions of the atmosphere and daylight, but nothing quite definite is known in this respect.

Carmine-lake is a substance of a beautiful red colour, and is obtained by the addition of an alkali to a decoction of cochineal mixed with alum. This substance was known before cochineal was discovered, and was made at Florence from kermes,—hence the name of Florentine lake, still in use. Cochineal is also met with in commerce in the state of cake. Although very rarely thus brought to Europe, a parcel reached France some years ago from Cordova, in South America: it was in the shape of solid, round, shiny, deep red-coloured cakes, containing five-sixths of the ordinary colouring matter of cochineal; the rest consisting of broken-up pieces of the insect (Coccus Cacti) mixed with vegetable matter.

Without being in the least adulterated, cochineal differs in richness of colouring matter, according to its origin. Sometimes parcels reach the European market which have been partly exhausted with boiling water and re-dried: this fraud is always accompanied by the loss of the naturallyadhering down of the insect, and in order to reproduce the appearance thereof the insects are, before, being quite dry, placed in casks along with some white powder or other,—as, for instance, white lead, sulphate of baryta, or French chalk. In order to detect this sophistication it is only requisite to place the cochineal in cold water for some time, when such adhering powders will become detached, sink to the bottom of the vessel, and may be analysed after decantation of the water. Partly exhausted cochineal is always more deeply wrinkled, and does not, when placed in water, take up moisture equally; a portion of the insects (grains, as they are termed by the brokers) float, and others become only partly submerged. Various methods have been proposed for determining the richness of cochineal in colouring matter. M. Robiquet does this comparatively in the following manner: -One part by weight of cochineal is five times successively exhausted with water, and the solutions obtained are decolourised by a solution of 10 parts of bleaching-powder: this method is obviously faulty, for the good reason that the decoction of cochineal contains other organic matters beside the colouring material, and the oxidising action of the hypochlorite of lime is partly expended upon these substances. By Anthon's method a known volume of a solution of alum is applied to precipitate completely a decoction of cochineal, and a standard sample of that ware is used for comparing the results. Penny's method is based upon the ready oxidation of the colouring matter of cochineal (carminic acid) by the red prussiate of potassium (ferricyanide) in the presence of an alkali; I grm. of pulverised cochineal is dissolved in 36 grms. of a weak solution of caustic potassa; this solution is diluted with 24 grms. of water, and there is next added by drops a standard solution of ferricyanide of potassium, containing 5 grms. of that salt to the litre of water, until the purplish-red colour of the original solution be converted into a brownish-yellow.

Since carminic acid is completely precipitated by neutral acetate of lead, M. Bloch proposes the use of a standard solution of that salt for estimating quantitatively the acid alluded to; unfortunately the reagent proposed precipitates a variety of other substances likewise.

Those who apply cochineal for dyeing test its goodness by a dyeing process, executed on the small scale, as for madder, taking 1 grm. of the ware; or they

print upon a woollen fabric a colour prepared with a known weight of pulverised cochineal: in both cases standard samples of the ware are applied for the sake of comparison. This method, however good, will give erroneous results if the cochineal is mixed with Brazil wood; but this sophistication may be detected, according to M. Persoz, by the following simple test:—When lime-water (not milk of lime) is added to a dilute solution (decoction) of cochineal the colour is discharged forthwith, but if Brazil wood is present along with the cochineal a violet tinge remains. When a piece of calico is impregnated with a decoction thus adulterated, and next steeped in a tepid solution of bichromate of potassa, the tissue will assume a rather deep colour, Cochineal is sometimes mixed with artificially-moulded insects, made up of some coloured paste; but this fraud is readily detected, even by steeping the suspected substance in water, which has the effect of disintegrating the moulded material, and making it crumble to pieces.

In the selection of cochineal considerable caution is needed. The grains should be full, plump, dark, and glossy. Silvery kinds and samples of a reddish-grey mottled appearance are not to be trusted, as the former are often weighted, and the latter immature and deficient both in the quantity and quality of their colouring matter. Gritty samples, in which small stones, clay, and sand are perceived, should be rejected. The specific gravity is an important characteristic, and may often be taken when there is not time to dye swatches, or to try the amount of colouring matter by any chemical procedure. We may at least lay down the rule, that though a light sample may be bad, yet a heavy one cannot be good. The specific gravity varies so much that of samples dried at 212° F. the superior kinds weighed 60 to 66 grs., whilst the same measure of the inferior qualities weighed 80, 90, and even 100. A Rham's specific-gravity bottle, or, in default, a very small light beaker, will answer the purpose. The vessel is accurately tared, and then filled exactly full of the cochineal, not by pressing, but by gentle tapping and shaking. If the same vessel is always used the results will be comparable.

A good lac-dye should be soft enough to be broken by the fingers. The fracture should be deep in colour, but should not appear shining and resinous, and should, when breathed upon, give out a strong and peculiar odour. If the lac is hard and has a resinous fracture, it is poor in colour and rich in shellac. It should pulverise easily under the pestle. Excess of resin is especially objectionable if the lac is intended for dyeing worsted goods which have to be hot-pressed. If it is loaded with resinous matter the pressing-paper will stick to the surface in patches, and can only be removed at a great outlay of time and labour, if at all. To ascertain roughly the amounts of resin, equal weights of the samples, in powder, are placed in small flasks, with the addition of equal measures of alcohol, and they are set to digest in a warm place, loosely stoppered, and occasionally shaken. The alcoholic solutions are then allowed to settle in the cold, decanted off into light capsules, previously tared, evaporated to dryness, and weighed. Or excess of water may be added to the alcoholic extracts, when the shellac will be precipitated, and its comparative amount may be judged by the eye with sufficient accuracy.

Cochineal is employed in dyeing and printing in the following states:—As met with in trade, without having undergone any preparation at all; ground

up to a more or less fine powder; in the state of decoction, made either with water only or with that fluid acidulated or rendered alkaline.

Carminic acid, although soluble in water, does not fix itself to any kind of fibre, whether animal or vegetable: it dyes cotton, mordanted with alumina only, amaranth-red, but when oxide of tin is simultaneously present as mordant a flat and meagre scarlet-red is produced; with iron mordants the colours produced are grey, violet-grey, or greyish-black, according to the strength.

Wool mordanted with preparations of tin is dyed a brilliant scarlet, of a peculiarly bright hue, and not readily obtainable by any other dye ware or upon any other fibre. The lac-dye of Messrs. Brooke, Simpson, and Spiller yields, upon wool, a colour almost as bright and beautiful.

Amaranth-red, red, violet-red, scarlet, and red-purple are produced by cochineal in its entire or ground-up state. Ammoniacal cochineal is used for mauve and amaranth-purple, and is, moreover, an ingredient of some composite colours. The dyeing of mordanted cotton, and all the operations pertaining thereto, are for cochineal the same as for madder.

Since carminic acid is rather a strong one, it has the power of dissolving temporarily some of the aluminous mordant, if too much of the ware is present along with the mordanted tissue: this would tend to weaken the colour intended to be obtained, and, moreover, the lake thus set free in the dye-beck might become fixed upon portions of the tissue intended to remain white; for this reason the cochineal is either added in two portions to the dye-bath, or the cloth is dyed first in a partly-exhausted bath, to which next a fresh portion of cochineal is added. The temperature of the first bath is only 40°; the second is brought to boiling; the addition of some nut-galls to the bath is intended to give fastness to the colour, as well as to prevent the corroding action of the carminic acid. Probably an excess of carminic acid forms a soluble acid carminate, which during the dyeing process is rendered neutral and insoluble, and thus fixed upon the white portions of the tissue. The goods, on being taken from the dye-beck, are so slightly soiled that after a thorough rinsing in water and a bran-bath the white is perfectly restored. The colours thus obtained are not fast, and do not stand washing with soap nor the action of either acids or alkalies.

Cochineal is very rarely, if ever, at all applied to mordanted cotton or calico tissues since the introduction of aniline colours; but its use as a steam-colour upon cotton, and in dyeing and printing wool and silk tissues, is very extensive.

Deep Rose-Red for Steam-Colour.—I litre of a decoction of cochineal made with 250 grms. of the grain to the litre; 2 litres of water; 0.5 litre of red liquor, at 10° B. (sp. gr. 1.075); 40 grms. oxalic acid; 1.75 kilos. gum.

Application-Red.—2 litres of a decoction of cochineal made with 375 grms. to the litre; 25 grms. tragacanth gum; 185 grms. pink salt, prepared with 1 litre of nitro-muriate of tin mixed with a hot and saturated solution of 500 grms. of sal-ammoniac.

Cochineal-lake is employed for the purpose of printing, being fixed by means of albumen. Cochineal is fixed upon wool and silk by means of alum and cream of tartar, whereby carmine shades are obtained; for scarlet, tin crystals are added.

The following are the shades obtainable by means of cochineal and ammoniacal cochineal upon wool:—

- I. Groseille* (bright).—For 10 kilos. of wool: 1 kilo. of cream of tartar and 2 litres tin solution, made up of 8 litres water, 400 grms. common salt, 1.25 kilos. tin, to which is gradually added 8 litres nitric acid. The wool is kept in this mixture, at boiling heat, for an hour, and is next dyed with ammoniacal cochineal for bright shades, in ammoniacal cochineal mixed with raw cochineal and some orchil for medium shades.
- 2. Violet Groseille.—Mordant as above, and dye with ammoniacal cochineal for clear as well as medium tints.
- 3. Amaranth-Red.—The same mordant; dye with raw cochineal and orchil for clear, bright, and medium tints; the quantity of orchil has to be increased for the latter. Deep shades are produced by the use of raw cochineal with orchil and sulphate of indigo.
- Red † is produced by the same process and ingredients as No. 3, only taken in varied quantity.
- 5. Vermillion.—Mordanting and dyeing are done simultaneously. For I kilo. of wool o'25 litre of the mordant for red is taken, and powdered cochineal, the dye-bath being heated to boiling.
- 6. Rose-colour.—Mordant as for No. 1, dyeing with ammoniacal cochineal.
- Bright Amaranth-Red.—Same mordant; dye, at boiling heat, with raw cochineal, ammoniacal cochineal, orchil, and for deeper shades some sulphate of indigo.
- 8. Violet Amaranth-Red is produced by the same means, only the quantities are somewhat varied.
- Purple is produced with the same mordant, the raw cochineal being applied at boiling heat.
- 10. Cherry-Red shades are produced by the same means, simply varying the quantities of materials.

The following may serve as examples for steam-colours upon wool:-

Rose-Reds.—(a). 16 litres of a decoction of ammoniacal cochineal (made up of 6 kilos. of ammoniacal cochineal, 2 kilos. acetic acid, and 12 litres of water, to be boiled together); alum, 1.5 kilos.; oxalic acid, 700 grms.; tartaric acid, 700 grms.; bichloride of tin, 1.5 kilos.; thickened with gum Senegal. (b). 500 grms. of ground cochineal, to be boiled with water, 12 litres to 9 litres; gum, 2.937 kilos.; oxalic acid, 500 grms.; bichloride of tin solution, at 55° Baumé (sp. gr. 1.618), 600 grms.

Ponceau Red.—2 litres of a decoction of cochineal containing 250 grms. to the litre; starch, 300 grms.; oxalic acid, 120 grms.; tin solution, 120 grms., made up with 1 kilo. of nitric acid, 2 kilos. of hydrochloric acid, and 360 grms. tin; 60 grms. of bichloride of tin.

Same colour, but different shade:—4 litres of decoction of cochineal containing 500 grms. to the litre; 3 kilos. gum; 350 grms. oxalic acid; 500 grms. of bichloride of tin solution (sp. gr. 1.618).

Amaranth-Red.—Exhaust 500 grms. of ammoniacal cochineal with pure water, evaporate to 2 litres, filter (or pass through a fine silken sieve); add

^{*} Since, technically, that word is in use in all languages to indicate that peculiar red exhibited by ripe red gooseberries, we retain it here also.

[†] Differs from that obtained by madder, but is a true red.

gum, 600 grms.; alum, 60 grms.; oxalic acid, 60 grms.—to this latter sometimes a little bichloride of tin is added.

Ammoniacal cochineal, mixed with various other substances, enters into the compositions used for some colours; for instance, with orchil, alum, and oxalic acid, in proper proportions, pomegranate-red is produced. With carmine of indigo, alum, and oxalic acid, violet is obtained.

The cochineal colours, especially upon cotton, are fugitive, and do not wear well. They are affected by washing, acids, or alkalies; soap suds and weak alkalies, lime-water, turn the colour to a violet-blue. They are also damaged by perspiration.

Silk is dyed carmine with cochineal by the following process:—(1), mordanting in a bath composed of 20 parts of water and ½ kilo. of bichloride of tin; (2), dyeing in a clear bath of cochineal, at a temperature of from 30° to 40°, the fabric being worked for about three hours: the shade may be improved by an addition of ammoniacal cochineal. For scarlet the silk is previously dyed yellow, with annatto. Silk is dyed ponceau by placing it in a bath prepared with 10 kilos. of ammoniacal cochineal dissolved in ten times its weight of water: this mixture is boiled for about ten minutes, and there is added to it, after that, ½ kilo. tin crystals, 1 kilo. of cream of tartar, 2½ kilos. of sulphuric acid, and 2 kilos. tin compound (viz., ½ kilo. tin, 1 kilo. hydrochloric acid, and 1 kilo. nitric acid): the whole mixture is boiled for an hour, decanted after cooling, and, after the addition of 3 kilos. of safflower, the silk is immersed in the liquid.

Harmala-Red.

The Syrian rue, known botanically as Peganum Harmala, is a plant growing plentifully in Western Asia and in the South of Russia. From its seeds is extracted a tinctorial principle known as Harmala-red. It is obtained by steeping the seeds of the plant in alcohol for from eight to fourteen days. The colour has basic properties; it is insoluble in water, but soluble in ether, and dissolves very readily in absolute alcohol. It combines with acids, forming red salts. Harmala-red dyes up a variety of shades upon wool and silk, from a bright rose to a full scarlet. The most suitable mordants appear to be the acetate and the sulphate of alumina. The harmala colours are not very fast. In the seeds of the Syrian rue there are also found harmaline and harmine, two alkaloids, soluble in acidulated water. They have been examined by several chemists, but have no tinctorial interest.

Erythrose.

Erythrose, or erythrosic acid, is the name given to a tinctorial substance prepared from the roots of rhubarb, as well the medicinal as the common kind. It is prepared by digesting the roots, previously cleaned, dried, and sliced, with 4 parts of nitric acid. The residue, which amounts to 8 to 10 per cent, dissolves in alkalies with red and purple colours. With the tin and aluminous mordants, erythrose may be made to yield pleasing shades, but it has never been brought into the market, and, since the discovery of the aniline colours, has been altogether lost sight of. Powdered rhubarb-root, rubbed up with an essential oil (bergamot, aniseed, or fennel) and magnesia, takes a bright rose-colour—a reaction which deserves to be further investigated.

Fustic-Carmine.

From fustic, yellow wood, or Cuba wood,—a dye-ware which will be more particularly noticed below, when we come to treat of yellow colouring matters,—a red dye may be prepared which is known as fustic-carmine. It is obtained as follows:—The extract of fustic is allowed to stand until the morine-lime is deposited, when the clear liquid is evaporated to dryness. The residue is finely powdered, and rubbed in a mortar with strong sulphuric acid. From the brown-yellow solution a brick-red mass separates, which gives a splendid carmine solution with a little ammonia or soda. It yields, with alum and a little alkali, a red precipitate; with protochloride of tin and chloride of barium, a red precipitate; and with nitrate of lead, a cherry-red.

This colour may be worth a closer examination than it has yet received. The raw material for its preparation may also be found by taking the deposit which is found on splitting blocks of fustic, and purifying it by repeated solution in boiling water, and crystallising. It is then dissolved in more boiling water with a little hydrochloric acid, and filtered. The clear liquor is set aside till a yellow powder subsides, which is then treated with sulphuric acid, as above.

PREPARATION OF LAKE COLOURS.

The increasing attention paid to the pigment-style in printing makes it necessary for us to give a brief account of the preparation of lake colours.

A. Red Lakes.

1. Madder-Lake.—The following is a receipt for which the Society of Arts awarded their gold medal to Sir H. Englefield, the inventor:—2 ozs. troy of the finest Zealand (crop) madder are inclosed in a bag of fine, dense calico, large enough to hold three or four times the quantity. A pint of pure water is poured upon it, in a Wedgwood or stone-ware mortar, and it is pressed and beaten with the pestle—taking care not to rupture the bag—as long as any colour can be expressed out of it. The liquid is then poured off. This treatment is repeated five times, with successive portions of water. The collected liquid is then heated to near boiling, in a silver or stone-ware vessel, and poured into a pint of boiling pure water, in which 1 oz. of alum—absolutely free from iron—has been previously dissolved. Into the mixed liquid 1½ fluid ozs. of a saturated solution of carbonate of potash is now gradually poured, with constant stirring. The product is washed, first by decantation, and then on the filter, and carefully dried. The yield is ½ oz.

Madder-lakes are at present generally made from charbon sulphurique, from garancin, or commercial alizarin. If garancin is used it is boiled in a block-tin pan with 20 times its weight of pure water, and alum, perfectly free from iron, equal to one-fourth or one-half the weight of the preparation of madder employed. The boiling is maintained for some hours. It is then allowed to settle; the solution, which is not quite clear, is drawn off; and the same operation is repeated three or four times with the former quantities of water and alum. The red extracts thus obtained are filtered, as quickly as possible, through flannel, but are preferably not mixed together. From the first, more saturated solutions, brown flakes are deposited in the course of a few days,

from which the very finest lakes can be prepared. For this purpose the clear liquid is drawn off with a syphon as far as possible, and the flakes are separated from the rest of the liquid by filtration. The clear liquid is used for the preparation of ordinary lakes. The precipitation of the colour is the next step: this can be effected by the addition of carbonate of potash or of soda, or caustic ammonia, with or without an admixture of tin-crystals. Chalk may also be used instead of the alkali, in which case gypsum is thrown down along with the alumina and colouring matter. If the whole of the alumina is thrown down the colour of the product is, of course, lighter. All lakes in which chalk is not employed have a smooth fracture. Each precipitant modifies somewhat the tone of the red produced. If a little salt of tin is added during the precipitation, or at its end, the fire of the lake is heightened, as the tin appears to prevent the precipitation of a trace of a yellow colouring matter. To retain this impurity in solution it is also well not to precipitate the whole of the alum. When the bulk of the alum has been thrown down, the lake is separated by filtration from the vellowish supernatant liquid.

To prepare the deepest madder-lakes, known as "crystallised" and "Munich" lakes, the above-mentioned brown flakes are dissolved in the smallest possible amount of caustic ammonia. The solution is filtered through linen covered with good filter-paper, and with this solution lakes of uncommon depth and brilliance can be prepared. The precipitation may be effected with alum, with salt of tin, or with a mixture of both, either warm or cold.

Splendid lakes can be prepared from artificial alizarin, and, doubtless, from

Perkin's artificial purpurin. (See also p. 268.)

2. Lakes of the Red Woods.—The chief points to be attended to in the preparation of these lakes are—That the decoction of the wood employed be not too recent; it must have been allowed to stand for some time, and to deposit certain impurities, before it can be used with advantage. The addition of a certain quantity of dilute solution of glue, or of carefully skimmed milk, is here advantageous. Alum, or tin-crystals, or a mixture of both,—of course in known quantities,—is then added, and the precipitation determined by means of alkaline carbonates, &c., as directed for madder. The common lakes are let down with starch, sulphate of lime, China clay, sulphate of baryta, &c. These articles are added during the precipitation, and greatly increase the yield of the lake at the sacrifice of its brilliance.

Lakes of a great variety of shades may further be obtained by the substitution of bismuth or antimony for tin and alumina.

3. Cochineal Lakes .- See pp. 359 and 360.

B. Blue Lakes.

A blue lake may be obtained by mixing a decoction of logwood, duly aged and clarified, with a little bichromate of potash, afterwards with a solution of sulphate of copper, and lastly with ammonia.

C. Green Lake.

Extract 1 lb. of raw coffee-berries with a gallon of pure water, and add a solution of 21 to 3 lbs. of sulphate of copper.

D. Yellow and Orange Lakes.

r. Annatto Lakes.—A yellow lake may be obtained by mixing the aqueous decocion of annatto with carbonate of soda, bringing the liquid to a boil, and then precipitating it with a solution of alum in excess.

An orange lake may be prepared from the same dye-ware by boiling it in carbonate of soda, and then precipitating with alum or salt of tin. A redder orange is produced by boiling the ware first in water, and rejecting the solution; boiling again in solution of carbonate of soda, and precipitating this latter extract with alum or salt of tin.

2. Fustic Lake.—Extract of fustic, which has been allowed to stand for a few days, is mixed with basic acetate of lead, stirring constantly.

Yellow lakes can be obtained from other dye-wares by processes similar to the above.

Aniline Lakes.

Dissolve in \(\frac{1}{4}\) kilo. of alcohol, at 95 per cent, 10 grms. copal and 1 grm. magenta. Filter, and add dry starch to form a uniform mass, dry, and powder. Other aniline colours may replace the magenta, giving a variety of colours.

Aurine yields a variety of beautiful precipitates if mixed with metallic and earthy solutions and thrown down by the cautious addition of an alkali. These, however, are not true lakes, but merely hydrated oxides, or sub-salts with which the aurine is mechanically incorporated. On washing with distilled water they lose their colour.

COLOURING MATTERS DERIVED FROM LICHENS.

Several kinds of lichens acquire a fine violet colour under the joint influence of ammonia and atmospheric oxygen. This fact, which depends on the presence of one or more peculiar principles, has been empirically known and applied industrially a long time before its theoretical explanation was discovered.

About the year 1300 a Florentine nobleman, named Federigo, discovered accidentally, while on a journey in the Levant, the colour-yielding properties of lichens; and Italy, especially Florence, supplied for more than a century the orchil manufactured with lichens from the Mediterranean. Afterwards the lichens were obtained from the Canary and Cape Verd Islands, and in our days they are imported from Madagascar, Zanzibar, Lima, Guayaquil, Angola, Madeira, Corsica, the Greek Islands, and Sardinia. The weeds belong to the genus known as Roccella, viz., tinctoria and fuciformis, and are distinguished as sea or marine orchil, because the plant thrives on rocks in the sea and along the sea-beach. These plants have a very short, circular base of implantation, from which issue several cylindrically-formed stems, ramifying like the branches of a tree, and terminating in fine points. Their specific characters vary, and so do their colours when dried, ranging from greyish-white to a brown. The richness in tinctorial matter, or rather in the principles capable of becoming pigments, varies even for one and the same kind, but certain tests enable the manufacturer to judge of the quality and purchase accordingly. The land lichens are met with on the naked rocks of the Pyrenees, Cevennes, Alps, and even the Scandinavian mountains, and belong to the genus Variolaria:—dealbata (Pyrenees), orcina (Auvergne), lecanora tartarea (Sweden): their exterior form is that of an irregular crust, exhibiting hardly any organised texture visible to the naked eye, which distinguishes them very readily from marine lichens. The entire plant was operated upon in the manufacture of orchil from land lichens. The process, as carried on about A.D. 1812, was described by M. Cocq.

In order to judge of the goodness of the material, a small quantity is put into a glass, and ammonia is poured over it. The good kinds become brown, but the useless, or at least inferior, qualities assume a yellow or green tint. The collected lichen is dried by being spread out in well-aired lofts.

For the preparation of the colour 100 kilos. of lichen are placed in a wooden trough, wider at the top than at the bottom, and the dimensions of which are as follows: Length 2 metres by a width of 1 metre, and a depth varying at the top from 0.06 to 0.07 metre and at the bottom 0.04 metre. This trough can be tightly closed by a wooden cover. To the lichen are added 240 litres of human urine, and this mixture is stirred up every three hours during two days and nights. There are added, on the third day, 5 kilos. of slaked and sifted lime, 125 grms. of powdered white arsenic, the same quantity of rock alum; whereupon the mixture is very frequently stirred. Fermentation sets in; forty-eight hours after another kilo. of lime is added, and the stirring is less frequently performed. The action is at end after the lapse of a month, when the product, which becomes better by keeping, is put into casks. The activity of the putrefied urine is due to the presence of carbonate of ammonia, formed by a well-known reaction from the urea. The lime is added in order to set the ammonia free and bind the carbonic acid: the orchil thus obtained is capable of yielding divers colours, viz., by simple treatment with boiling water amaranth is produced, and the intensity of this colour is entirely modified by the lapse of time the woven fabrics are left in the bath, so that at last a brown may be obtained. One of the first improvements in this branch of industry is the substitution of ammonia for the mixture of urine, lime, and arsenic, by which means time is economised and the whole process better regulated. The use of lime was, moreover, found to be rather injurious to the process.

The principal forms in which these colours are now found in commerce are orchil paste, orchil liquor, cudbear, and "French purple." The paste and liquor are distinguished as "red" and "blue," according as they incline to either of these colours. Cudbear, known on the Continent as persio, is a dry powder, and, from the mode of its preparation, is of a reddish cast. The manufacture of these dyes will be described below.

Since the colouring matter of orchil is soluble in water, that liquid has been employed to extract it from the orchil weeds,—an operation similar to the preparation of dye-extracts from the woods, with this difference, that the latter contain the colours ready formed, while in the former it has to be developed. In this way single and double extracts of orchil, and orchil lakes, may be obtained.

The colourable material of the lichens is not uniformly distributed through the plant, but is chiefly deposited as a greyish powder on the surface, easily detached by mechanical means. M. Frezon has turned this observation to account, by submitting the lichens to the joint action of friction and water

upon a sieve; a whitish starch-like powder is thus obtained, which, on being treated with ammonia, yields a colour far purer and more beautiful than that obtained by the maceration of the whole weed.

Before we can further enter into the details of the orchil manufacture, we have to turn our attention to the remarkable discoveries made by chemists in this field, since upon these the improved methods of applying the lichens as dye-materials are based.

Chemical History of the Colouring Matters of Lichens.

M. Robiguet succeeded, in 1849, in extracting from the Variolaria dealbata a colourless, crystalline, saccharine, yet astringent, substance, which he termed orcine. He found, also, that orcine, under the influence of air and ammonia, fixes nitrogen, and becomes converted into a violet-coloured matter. The composition of orcine and of the orceine thence derived were investigated by Dumas, who also found the clue to the precise reaction which accompanies the formation of orceine from orcine. Kane proved that orceine is not the only colouring substance formed by the transformation of orcine. The researches on this subject carried out by Heeren, Schunck, Stenhouse, Rochleder, Hesse, De Luynes, Menschukine, Grimaux, and others, have led to the discovery and examination of several acids pre-existing in the lichens, which, under varying conditions, split up into orcine and other substances of no industrial moment. From these researches we learn that the existence of ready-formed orcine in the lichens is the exception, since it is only formed when the lichens are treated, and as soon as developed it is further modified.

Although the chemical history of these acids is not fully elucidated, they have been sufficiently studied to admit of their rational formulæ being established and their relations indicated. The acids are—

- r. Erythric acid, or erythrine, C₂₀H₂₂O₂₀, yielding, as immediate derivatives,—(a), picroerythrine, C₁₂H₁₆O₇; (b), orsellic acid, C₈H₈O₄: picroerythrine splits up into—(a), erythrite or erythromannite, C₄H₁₀O₄; (b), orsellic acid, which in its turn is split up into carbonic acid, CO₂, and orcine, C₇H₈O₂.
- Lecanoric acid, lecanorine, α or β orsellic acid, di-orsellic acid, C₁₆H₁₄O₇;
 it is decomposed into orsellic acid, C₈H₈O₄, without production of
 erythrite or picroerythrine.
- 3. β-Erythrine or β-erythric acid, C₂₁H₂₄O₁₀, a higher homologue of erythrine: its products of decomposition are (a), orsellic acid; (b), β-picroerythrine, C₁₃H₁₆O₆, which differs from its homologue, picroerythrine, C₁₃H₁₈O₇, by having H₂O less: it (viz., the β-picroerythrine) is split up into erythrite and a mixture of carbonic acid, and β-orcine, C₈H₁₀O₂, which, by combining together, form β-orsellic acid,—that is to say, a higher homologue of the orsellic acid: β-orcine is a homologue of orcine.
- Evernic acid, C₁₇H₁₆O₇, the superior homologue of lecanoric or diorsellic acid; it is decomposed into orsellic and evernic, or β-orsellic acid, the homologue of the first, C₉H₁₀O₄.
- 5. α and β Usnic acids, isomeric with and homologues of evernic acid, $C_{18}H_{18}O_7$; it is also called di- β -orsellic acid. Since it yields, when

split up, β -oricine, we may admit that it might produce β -orsellic or evernic acid.

6. Roccellic acid, C17H32O4.

7. Roccelline, C18H16O7.

8. Parelline, or parellic acid, C₉H₆O₄: the two last-named bodies are not very well known.

Erythric acid, or Erythrine, C20H22O10, was discovered by M. Heeren, and fully investigated by Drs. Schunck, Stenhouse, Hesse, and De Luynes. It occurs in most of the orchil lichens, and especially in the species known as Roccella tinctoria, fuciformis, and Montagnei. This acid is insoluble in cold water, soluble in 240 parts of boiling water, whence, on cooling, it is deposited in the crystalline state. It is more readily soluble in alcohol and ether, boiling alcohol being its best solvent. On cooling, the solution deposits groups of crystals. The alcoholic solution is neutral to test-paper, colourless, inodorous, and tasteless. Erythrine is dissolved by strong sulphuric acid in the cold, and by hot hydrochloric acid; the former solution is precipitated by cold water. Caustic and carbonated alkalies, and the hydrates of baryta and lime, dissolve erythrine readily, whilst acids precipitate the substance unaltered, in the shape of a white, bulky, gelatinous mass; but if the alkaline solutions have been boiled, or kept for a long time, this precipitation does not take place, since erythrine is then altered in a peculiar manner, which we shall presently describe. The ammoniacal solution reddens on exposure to air; with perchloride of iron a purplish colouration is produced. magnesia-solution of erythrine (erythrite of magnesia) is precipitated by neutral acetate of lead, but the alcoholic solution of erythrine is not precipitated by that reagent; it is, however, thrown down by basic acetate of lead. When erythrine is for a length of time boiled with water it fixes the elements thereof, giving rise to the formation of picroerythrine, carbonic acid, and orcine. This reaction is performed in two periods, during the first of which picroerythrine and orsellic acid are generated, while during the second the orsellic acid is split up into carbonic acid and orcine. If, instead of water, alcohol or wood spirit (pure methylic alcohol) is taken, orsellate of ethyl and orsellate of methyl are produced. Alkalies, especially if aided by heat and lime, greatly favour the transformations of erythrine.

Dr. Schunck prepares erythrine by exhausting the lichens with boiling water; the crystalline powder deposited on cooling is purified by the recrystallisation from alcohol. By this method a portion of the product is modified, and converted into orcine and picroerythrine, whence it is preferable to treat the lichens with milk of lime in the cold. The calcareous solution thus obtained is treated with carbonic acid, whereby carbonate of lime and erythrine are thrown down. This mixed precipitate is next treated with tepid alcohol, and the solution first purified by means of animal charcoal, and, when decolourised and still hot, so much water is added to the alcoholic solution as to produce a permanent turbidity: on cooling, the erythrine is thrown down in a crystalline form.* The calcareous solution may also be precipitated by hydrochloric acid. When the lichens are exhausted with cold weak ammonia a yellow liquor is obtained, containing erythrine and roccellic acid, the latter being a kind of fatty matter, insoluble in water, but soluble in

^{*} Hesse, "Annalen der Chemie und Pharmacie," vol. cvii., p. 297.

alcohol, ether, and ammonia. These two substances are separated either by precipitation with hydrochloric acid, and subsequent solution of the erythrine in hot water, or by adding chloride of calcium to the ammoniacal liquor, whereby the roccellic acid is separated as insoluble roccellate of lime. Since, however, ammonia also dissolves a brown matter present in the lichens, the purification of the erythrine is not so easy as when milk of lime is used.

Bromine converts erythrine, in presence of ether, into a crystalline bromated product, insoluble in water, but soluble in alcohol.

Picroerythrine, C₁₂H₁₆O₇, is a solid, white, very bitter body, sparingly soluble in cold water, readily soluble in boiling water; soluble, also, in alcohol and ether. It may be obtained from its concentrated aqueous solutions in crystals; it fuses at 158°; its reaction with test-paper is slightly acid, With bromine, in presence of ether, it yields a bromated compound. If heated in a sealed tube, orcine is formed. It is soluble in alkalies in the cold; its ammoniacal solution reddens easily on exposure to air. Neutral acetate of lead does not yield a precipitate with picroerythrine, but with the basic acetate a precipitate is produced containing 68.94 per cent of oxide of lead; perchloride of iron gives a purple colouration; ammoniacal nitrate of silver is reduced to the metallic state. Prolonged boiling with water does not affect picroerythrine, but if, at the same time, baryta or lime is present in excess, water is fixed, orcine, and erythrite, and an alkaline earthy carbonate are formed. This reaction is greatly accelerated at 150°, in sealed tubes. Picroerythrine is obtained by boiling erythrine with water, when it dissolves gradually, and the concentrated liquid yields a brown glue-like mass, which gradually becomes crystalline; on treating this mass with cold water impure orcine dissolves, while picroerythrine remains as a residue. Instead of water alcohol can be taken, and, according to Dr. Stenhouse, erythrine should be treated with lime previous to boiling, in which case the conversion is far more rapid.

Erythrite Synonyms:— Erythroglucine, erythromannite, pseudo-orcine, C₄H₈O₄. This substance is an important member of the group, inasmuch as the researches of Dr. Hesse and De Luynes have proved that erythrite acts as a tetratomic alcohol, of which erythrine and picroerythrine are the orsellic ethers; orsellic acid is itself triatomic, and its rational formula is, according

to Dr. Grimaux, ${}^{C_8}_{H_3}{}^{H_5}{}^{O}_{3}$.

Without entering here into hypothetical details, we prefer to mention the process of preparation of erythrite and orcine as suggested and carried out by M. de Luynes. Lima lichens are exhausted with milk of lime, the filtered liquid is precipitated with hydrochloric acid; the erythrine thus obtained is washed, and next heated for two hours in a closed iron vessel, at 150°, along with a certain quantity of milk of lime, too small to effect the entire decomposition of the substance: the carbonate of lime having been separated by filtration, the liquid is evaporated slightly, when, on cooling, orcine separates in the crystalline state; the evaporation of the mother-liquor yields a crystalline magma, consisting of erythrite and orcine, which latter is removed by means of ether. The erythrite is purified by solution in boiling alcohol, from which it crystallises on cooling. The calcareous extract may also be boiled, in order to concentrate it; the lime may be removed by carbonic acid; the liquid, after removal of this deposit, is evaporated to dryness, and treated with ether to remove the orcine.

Erythrite yields large crystals belonging to the tetragonal system, somewhat sweetish to taste, neutral to test-paper, very soluble in water, less so in alcohol, almost insoluble in ether; it does not assume any colour, either by the combined action of air and ammonia, or when in contact with hypochlorite of lime. It is neither precipitated by basic nor neutral acetate of lead. It fuses readily, and does not possess the colourable properties of the lichens. It is decomposed by caustic potassa, yielding hydrogen and acetic acid, and when heated to 240°, with that base, hydrogen and oxalic acid are formed. When treated with from 20 to 30 parts of concentrated sulphuric acid, at 60°, erythrogluci-sulphuric acid is formed: the aqueous solution of this substance is readily and rapidly oxidised when in contact with air or with spongy platinum. When dry erythrite is fused, and heated along with twelve times its weight of hydriodic acid (sp. gr. 1'99), it yields, on distillation, hydriodate of butylen, C₄H₈IH.

Orsellic, or a-Orsellinic, Acid, C₈H₈O₄.—Since orcine is diatomic, and differs from orsellic acid by having CO2 less, the orsellic acid is, according to Grimaux, triatomic. This acid is best prepared by boiling the lecanorates of lime or baryta for a short time with water; the ebullition should be carefully conducted, since otherwise carbonate of lime and orcine are formed: the orsellic acid is precipitated by means of hydrochloric acid; the ensuing gelatinous precipitate is treated with boiling alcohol or with warm water, and, on cooling, prismatic crystals are deposited. This acid is more soluble in water than diorsellic and lecanoric acids; its lime and baryta salts are also more soluble, and it is by far more soluble in ether; its taste is sour and bitterish; it reddens litmus-paper; fuses at 176°, but is then also decomposed into orcine and carbonic acid. This reaction is also produced by long-continued boiling. Bleaching powder gives it a fugitive violet-red colour. In contact with air, caustic ammonia colours it red. The alkaline and alkaline-earthy orsellates are soluble in water, but if any excess of base be present are readily decomposed into orcine and the carbonate of the base. Orsellic acid, combined also with methyl, ethyl, and bromine, converts it into tribromorcine.

Lecanoric, Diorsellic, α -Orsellic Acid, or Lecanorine, $\begin{pmatrix} C_8H_5O \\ C_8H_5O \\ H_4 \end{pmatrix}$ O_5 .

-Schunck found this acid in lichens belonging to the species Lecanora and Variolaria, Rochleder and Held in the Evernia prunastri, and Stenhouse in the Roccella tinctoria. It may be prepared by the following process:- The lichens, previously pulverised, are exhausted with ether, the solution is evaporated to dryness, and the residue first treated again with ether, next with water, and lastly dissolved in alcohol. The lichens may also be treated with milk of lime or with ammonia, the liquids filtered from the insoluble residue, and the filtrate treated with hydrochloric acid; the pasty precipitate is separated by filtration, well washed, dried, and next taken up with alcohol, from which the acid crystallises. This acid then forms white acicular crystals, sparingly soluble in cold water and cold alcohol; soluble in ether, boiling alcohol, and acetic acid: I part of the acid requires for solution 2500 parts of boiling water, 150 parts of alcohol at 15°, 5.15 parts of boiling alcohol, and 80 parts of ether. Bleaching-powder colours it temporarily red. The alcoholic solutions of the acid are tinged purplish by the addition of chloride of iron. When the acid is dissolved in ammonia, and left in contact with air, it

assumes gradually a violet-red. If boiled along with water and an excess of lime and baryta, first an orsellate is formed, which is, in its turn, when the process is continued, decomposed into carbonic acid and orcine. The substance known as α -orcine, or simply, also, orcine, first discovered by Robiquet, is the colourable material of the lichens, or rather it is—among the ultimate products of the splitting up of the acids just mentioned—the only substance capable of conversion into a colouring matter. It is not proved, and does not appear probable, that the colouring matter which is the result of the simultaneous action of air and ammonia upon orcine is identical with the colouring matters which ensue by the ammoniacal oxidation of the colourable acids (viz., erythrine, lecanoric, orcellic, and picroerythrine). Indeed during the manufacture of orchil by the ordinary methods there are formed several colours, all exhibiting different tones.

Pure orcine forms colourless prismatic crystals, belonging to the monoclinic system.* It is very readily soluble in water and alcohol, and soluble in ether; from its aqueous solutions it crystallises with one equivalent of water, but the ethereal solution yields anhydrous crystals. Orcine has a sweetish, but at the same time a disagreeable, taste. Its hydrate fuses at 100°, losing its water of crystallisation; but in the anhydrous state it may be distilled at 290°, and sublimes without decomposition when not submitted to this experiment in large quantity at once. The formula of orcine is C₇H₈O₂+H₂O, the latter eliminable at 100°, or over sulphuric acid in vacuo, being water of crystallisation. Though orcine is neutral to test-paper, it behaves in some instances as an acid, so that in a state of fusion it decomposes alkaline carbonates, and precipitates silica from alkaline silicates; orcine precipitates the quinine salts, entering into a peculiar combination with that base. Solutions of orcine are not precipitated by bichloride of mercury, neutral acetate of lead, sulphate of copper, tannin, and gelatin, but yield with basic acetate of lead a white, and with chloride of iron a deep red, precipitate. Orcine reduces salts of gold and silver to the metallic state, if ammonia is simultaneously present. Orcine combines with chlorine and bromine; if thrown into fuming nitric acid which is kept cool, it dissolves therein without giving off nitrous vapours. This solution is precipitated by water, yielding a red substance soluble in alkalies. When crystallised orcine is placed under a bell-jar, close to a vessel containing nitric acid (sp. gr. 1.384), it becomes first brown, and then red. This change proceeds for some days. The substance thus produced differs essentially from orcine; it dyes silk and wool red, without requiring any mordant. Ammonia changes this colour temporarily to a violet; fixed alkalies do so permanently, but acids restore the original colour.† On treatment with a large excess of concentrated sulphuric acid, and exposure to a temperature of from 60° to 80°, orcine becomes black. If water is added to the acid after cooling, and the liquid saturated while cold with carbonate of lead, then filtered, and the clear filtrate concentrated by evaporation, a crystalline mass is obtained which, if treated with ether, yields orcine. On dissolving the residue in boiling water, re-treatment with carbonate of lead, filtering again, and setting aside the liquid, it yields brownish crystals of basic orcino-bisulphate of lead,

^{*} Laurent and Gerhardt, "Annales de Chimie et de Physique" [3], vol. xxiv., p. 317. Miller, "Ann. der Chem. und Pharm.," vol. lxviii., p. 99.

[†] De Luynes, "Comptes Rendus de l'Académie des Sciences," vol. lvi., p. 715.

with a nacreous reflection. Contact of air and sunlight tend to redden orcine gradually; bleaching-powder colours it first a deep violet, but which turns gradually to a brown, and becomes finally yellow. Under the influence of fixed alkalies orcine absorbs oxygen very rapidly, and assumes a red or brown colour. Vapours of ammonia convert orcine into a deep brown substance, orceine; bichromate of potassa, either with or without addition of sulphuric acid, converts orcine into a brown substance, while the prolonged action of nitric acid, aided by heat, produces oxalic acid.

Orcine may be prepared by various processes. Robiquet obtained it by exhausting Variolaria with boiling alcohol: this liquid deposits, on cooling, crystals, which are first removed, after which the fluid is evaporated to dryness. The dry residue, treated with boiling water, yields, on concentration, crystals of orcine. Dr. Schunck boils lecanorate of baryta with water for a long time; carbonate of baryta is precipitated, while orcine remains in solution, and is purified by repeated crystallisation. Dr. Stenhouse extracts the lichens in milk of lime, boils and concentrates the liquid, precipitates the lime by carbonic acid, evaporates the liquid to dryness, and takes up the residue with concentrated boiling alcohol. The crystals of orcine which separate from this liquid, on cooling, are re-dissolved in pure anhydrous ether. The best process for preparing orcine is that above described, as devised by M. de Luynes. Dr. Stenhouse has extracted from the Roccella tinctoria, of the Cape of Good Hope, a substance termed roccellinine, by the following process:—The lichen is treated with a cold milk of lime, the liquor is filtered, and next precipitated by hydrochloric acid; the ensuing pasty white precipitate is first washed with water, and next boiled with alcohol: this procedure causes the formation of orsellate of ethyl, which is soluble in boiling water, while the unaltered roccellinine is not thereby dissolved, and may be separated.

Roccellinine is soluble in ammonia and alkalies, but these solutions do not become coloured on exposure to air; it is almost insoluble in alcohol and ether when cold, but the boiling alcoholic solution deposits, on cooling, silky needle-shaped crystals, which, according to Dr. Stenhouse, consist of C₁₈H₁₆O₇.

Parelline, or Parellic Acid, according to Dr. Schunck, accompanies lecanoric acid. In order to obtain the former acid, lichens are exhausted with boiling alcohol, and the liquid thus obtained boiled for some time, and next evaporated to dryness. The residue is taken up in boiling water, to dissolve the orsellate of ethyl; the residue is treated with boiling alcohol, from which the parellic acid separates, on cooling, in the shape of fine crystalline needles, insoluble in water, but soluble to some extent in cold alcohol and ether. This substance, $C_9H_6O_4$, it appears, does not yield, when treated with ammonia and in contact with air, any red or violet matters.

Colouring Matters of Orchil.

Although there is no doubt that in the dye known as orchil several different pigments exist, only one of these, viz., orceine,—formed according to the researches of MM. Robiquet and Dumas, at the expense of orcine,—has been closely investigated. This orceine requires for its formation two conditions:—the presence of atmospheric oxygen and that of ammonia, while a temperature of from 30° to 50° favours its generation. When orcine in a crystal-

lised state is exposed to the action of ammoniacal vapours this conversion takes place, and equally so when an aqueous solution of orcine containing from 10 to 20 per cent is exposed to the action of these vapours: time is a very essential item in this process. According to M. Dumas, the formula of orceine is $C_7H_7NO_3$, and the formation of this substance from orcine may therefore be elucidated by—

 $\underbrace{C_7H_0O_2 + NII_3 + O_2 = C_7H_7NO_3 + H_2O}_{Orcine.} + H_2O.$

Dry orceine is a brown powder, somewhat soluble in water, to which it imparts a red colour. The neutral alkaline salts precipitate this solution. Orceine is insoluble in ether, but very readily soluble in alcohol, giving a scarlet solution; alkalies and ammonia also dissolve it, vielding magnificent purplish-violet solutions. Orchil as met with in commerce exhibits, under similar conditions, the same phenomenon; it is essentially orceine in combination with ammonia (orcineate of ammonia), which yields, when dissolved in water with various metallic salts, diversely coloured precipitates or lakes, but after drying the colour of these bodies is very faint. Orcineate of ammonia is decolourised by reducing agents, as, for instance, by boiling along with water and metallic zinc, or addition of sulphydrate of sulphide of ammonium, but the colour reappears on exposure to air. When an ammoniacal solution of orceine is acidified with hydrochloric acid, and zinc added, the fluid is decolourised. The addition of ammonia to this liquid causes the precipitation of a flocculent white matter, leucorceine, which, on exposure to air, becomes violet and purplish. Chlorine converts orceine into a yellowish-brown matter, chlororceine. Orceine is, by itself, a red substance, which, under the influence of alkalies, becomes violet, but acids restore the primitive red colour.

Dr. Kane has found, in the orchil of commerce, two other red matters, orceine and azoerythrine, and, moreover, a semi-fluid purplish substance, erythroleic acid. The azoerythrine, $C_{TI}H_{I9}NO_{TI}$, is insoluble in water, alcohol, and ether, but soluble in alkalies, to which it imparts a wine-red colour; erythroleic acid, $C_{I8}H_{II}O_4$, is soluble in alcohol, ether, and alkaline solutions, but insoluble in water. These products have not been, however, sufficiently investigated.

New Methods of Preparing Orchil.

The researches above mentioned, more especially those of Drs. Schunck, Stenhouse, and Rochleder, have led to great improvements in the manufacture of orchil, especially in this respect—that the colourability of the lichens is not a property of these plants as a whole, but is due to some principles therein contained, which are capable of being rendered soluble by suitable reagents, or may be set free by mechanical means. These colourable materials form only a very small portion of the total weight of the lichens. The chemical operations are, moreover, rendered easier and more manageable if the large bulk of ligneous matter is removed.

We have already observed that Frezon utilises the slight adherence of the erythrine and the lecanoric acid, which are chiefly on the surface of the plants, in order to isolate and detach these substances. This is effected as follows:—The lichens, previously sorted and washed several times with cold water, are ground up to a somewhat liquid paste. This paste is exhausted by washing several times with cold water; the liquids obtained are filtered

through a peculiar kind of loosely-woven, felty, woollen tissue, which retains the ligneous matter, but admits of the passage of the partly dissolved, partly suspended colourable acids. By the addition of a small quantity of bichloride of tin, the colourable matters are coagulated, and collected on filters made of stout linen tissue. After having been once more washed with water the mass is dissolved in ammonia, and placed in properly constructed tanks, wherein, by the aid of a proper temperature and frequent stirring, the material is converted into orchil, an operation which requires a long time. The progress of this operation is tested by dyeing, with a certain weight of the orchil, a certain size of woollen tissue. By this means, also, the end of the operation—that is to say, the period of highest intensity of colouration—is ascertained.

M. Gauthier de Claubry has observed, and very properly so, that the prolonged contact of the lichens with water has the effect of rendering the colourable matter soluble, so that, unless the operations described are carried on very rapidly, a loss may be sustained.

Dr. Stenhouse suggests that the lichens should be treated, at the spots where they are collected, with milk of lime, 30 per cent of lime of the weight of the lichens; the liquid filtered, precipitated with hydrochloric acid, and the white pasty precipitate filtered off, which, after having been washed and dried, should be conveyed to the orchil manufacturers, since it contains in small bulk all the really valuable matters of the lichen, while the expense of transport would become less. The great objection to this plan is, that (while it might otherwise be also employed in the manufacture of orchil from the lichens brought to Europe) in contact with lime the erythric and lecanoric acids are very rapidly altered, and the matter spoiled, so that even so short a maceration with lime as three hours is injurious. Ammonia might be used to extract from the lichens the colourable acids, but the paste obtained by precipitation with hydrochloric acid is yellowish-brown, owing to the ammonia simultaneously dissolving a peculiar brown matter present in the lichens. Moreover, the same objection as for lime holds good for the use of ammonia. When the colourable principles of the lichens are extracted by prolonged boiling, with either water alone or water to which an alkaline substance (any alkaline phosphate, borate, carbonate, or also any caustic alkali) is added, the conversion of the insoluble substances precipitable by acids into soluble matters no longer precipitable is rapidly brought about, and therefore the liquids have to be concentrated by evaporation.

The ordinary method of preparing orchil paste is as follows:—The apparatus used is a wrought-iron horizontal cylinder, made very smooth within, about 6 feet in length and 3 feet in diameter. The lowest third part of the circumference, for the entire length, is fitted with a steam-jacket for the application of heat. A shaft runs through the cylinder axially from end to end, fitted with paddles and worked by steam-power, in order to agitate the mass. Along the top runs a slit from end to end, with a movable lid, for introducing the charge of weed and ammonia. There are also a few small slides for regulating the supply of air. In the front of the cylinder, below the axle of the agitator, is a man-hole, for discharging, and above the axle, right and left, are two small slides for the admission of air. A cylinder, of the dimensions given, is charged with 180 lbs. of weed and 540 lbs. ammonia, at 5° of the common ammonia-glass, which corresponds almost exactly with Baumé's

hydrometer for liquids lighter than water. The charge can be ready in three days, but the quality is improved if worked for a week. Steam is admitted into the casing by a pipe at the end opposite to the man-hole, and the temperature is kept up at such a height that the paste feels slightly uncomfortable to the hand—about 60° C. or 140° F. The agitator is kept gently revolving all the time. The admission of air is regulated according to the judgment of the manufacturer. The yield, for the quantity given above, is 540 lbs., or three times the weight of the weed employed. An excess of ammonia renders the colour less stable, impairing its affinity for the fibre. It should be mentioned that the blue shade makes its appearance first, and by proper management the change can, if desired, be arrested at this point. The red shade appears when the joint action of air and ammonia is allowed to proceed to a greater length.

To prepare orchil liquor the weeds are boiled out with water, and strained; the extract concentrated to 8° to 10° Tw., and then heated and agitated with ammonia at 24° of the ammonia-glass. Continual agitation is here not necessary. The arrangements for extracting the weed are various. It is generally boiled in three successive waters, the first and second liquors being mixed and concentrated, whilst the third serves for the first extraction of a fresh quantity of the weed. The weeds for paste and liquor should not be ground too fine, being bruised under edge-stones rather than pulverised. Certain additions are frequently employed by manufacturers. Small quantities of red prussiate (ferricyanide of potassium) give the orchil a redder tone, whilst a slight addition of a fixed alkali—generally carbonate of potash—serves to give an extra blue shade. An improved bloom and brilliance is imparted by a little tartar, or white argol.

The manufacture of cudbear is very simple. Orchil paste, made as above described, is dried at a steam-heat, and afterwards ground to a fine powder in a lac-mill. It is very generally weighted with common salt, and its appearance is often factitiously improved by the addition of a little magenta.

Orchil paste varies greatly in quality, from variations in the lichens used in the manufacture, from the degree of care and skill used in the process, and from the presence or absence of impurities. It may be too watery, containing not more than 20 per cent of solid matter, in which case an extra quantity is needed to produce the shades required. The amount of moisture is readily found by weighing out a quantity, and drying, at the heat of boiling water, till no further loss is experienced, and then weighing the residue. Orchil may have been overdone with ammonia, in which case its affinity for the fibre will be feeble. If a cask of orchil paste, when first opened, gives off a pungent ammoniacal smell, it may be pronounced faulty, but time and exposure to air will correct this defect. Practical men often judge the quality of an orchil paste by rubbing a little on the back of the hand, and permitting it to dry. If the colour is well made a stain will remain on the skin, which cannot readily be removed by washing in cold water or rubbing with a cloth. If the colour is bad, and especially if it be too ammoniacal, it is easily washed off with cold water.

Orchil is sometimes fraudulently mixed with extracts of logwood, sapan, &c. To detect these, about 50 grs. of the suspected sample are stirred up in 3 ozs. of water; 50 drops of a solution of protochloride of tin, made by

dissolving tin crystals in double their weight of water, is then added, and the whole is brought to a boil. A pure orchil gives only a faint yellowish colour. The presence of logwood is shown by a greyish-blue residue, whilst sapan or peach-wood is indicated by a reddish tinge. The actual beauty and tone of different samples of orchil can only be ascertained by dyeing swatches of some suitable material—such as white camlet, French merino, or flannel—with equal weights of the samples under examination, under circumstances quite similar.

Orchil liquor is used in dyeing wool and slubbings which could not readily be freed from fragments of the weed if the paste were employed. Liquors range in strength from 8° to 20° Tw. They are best tested by dyeing comparative samples.

Cudbear, in addition to salt, is sometimes adulterated with ground chalk. These impurities may be detected by burning a weighed quantity to ashes. If genuine, the residue will be inconsiderable. Or swatches of a white woollen or worsted material, equal in weight, are dyed with equal weights of the samples.

Since the year 1857, MM. Guinon, Marnas, and Bonnet have obtained from lichens a product known as pourpre Française, which yields not only an extremely beautiful and brilliant but fast dye-material. This dye-material is prepared as follows: - The lichens are treated with a cold ammoniacal liquid, whereby the colourable acids are dissolved. After having been in contact with this fluid only for a few minutes, the lichens are placed on a filter, in a bag, which is squeezed very strongly, the filtered liquid is precipitated with hydrochloric acid, the ensuing precipitate is filtered, washed and left to drain, and next dissolved in ammonia, and left exposed to the action of air in the cold. Up to this part of the proceedings there is no difference from the ordinary method of orchil making, but instead of allowing the process to go on until the peculiar colour of orchil is completely developed, the moment when the liquid mass becomes a cherry-red is watched, and, as soon as that point has been reached, the material-semi-fluid, or thickish fluid-is brought to ebullition, which is kept up for some time. It is then run into flat-bottomed, rather shallow vessels, of from 2 to 3 litres capacity each, so as to form layers of from 5 to 6 centimetres in thickness: these vessels and contents are heated to from 70° to 75°, in a properly constructed stove-room: the operation is finished when the liquid has assumed a beautiful purple tint, and does not, when painted over a sheet of white paper, change its colour after drying. The purple matter thus obtained is accompanied by a red acid, which alters its beauty. In order to eliminate that acid chloride of calcium is added, when a precipitate, or lime lake, is obtained, which, after having been filtered, washed, and dried, appears a bluish-purple mass, and when rubbed with the finger-nails assumes a cupreous hue. By fractional precipitation lakes of different shades are obtained. The mother-liquor retains, beside some of the purple, a red substance, which may be applied to dye pomegranate-colour on silk, and is also a fast colour.*

Instead of a lime lake an alumina lake may be prepared by employing alum for the precipitation of the ammoniacal solution. By treating the lime lake of the pourpre Française with an equivalent quantity of oxalic acid, and

^{*} J. Persoz, "Répert. de Chim. Appliq.," vol. i., p. 189.

exhausting afterwards with boiling alcohol, the purple matter is obtained, when the alcoholic liquid is evaporated in the shape of crystals. This substance has not been as yet chemically investigated. The price of this French purple was at first 200 francs (£8) per kilo.; it has come down to 80 francs (£3 5s.), and is distinguished from ordinary orchil by not being reddened by vegetable acids.

The researches made by M. Gauthier de Claubry have proved that the production of French purple is mainly due to that portion of the process (the stoving) and the keeping up thereby of a very uniform temperature. The same chemist also ascertained that when orchil is prepared at 60° a product is obtained yielding more solid dyes than when manufactured at lower temperatures. Although the process of making orchil is known in its general features, every individual manufacturer keeps his own peculiar process and everything relating thereto secret. The quantity of colourable matter of the lichens can vary from 21 to 12 per cent. In order to ascertain comparatively the tinctorial value of the various samples equal weights thereof (100 grms.) are macerated for a short time - a few minutes - with milk of lime; the liquid is placed on a stout cloth, filtered, squeezed, and precipitated by means of hydrochloric acid; the resulting white paste is placed on a small silk sieve, rapidly washed, well drained, and weighed. Dr. Stenhouse applies a standard solution of bleaching-powder, which, on being added drop by drop to the calcareous lichen extract, causes first the production of colouration, and as soon as that has attained its summit decolouration ensues; by comparing the degrees of solution of hypochlorite required for the production of these phenomena in different solutions of lichens their goodness may be approximately estimated.

Another process is to exhaust 100 grms. of lichens with water rendered alkaline; this liquid may be concentrated by evaporation to 100 grms., and the coloration may be caused by the addition of 30 grms. of ammonia. In other terms the orchil manufacture is executed on the small scale; a dyeing process with unmordanted wool will give some idea of the quantity of colouring matter formed. The manufactured article, orchil, is tested by a dyeing process with unmordanted wool; for a piece of that material 5 centims. long by 2 centims. wide from 0.5 to 1.0 grm. of orchil and 300 grms. of water are taken. These materials are put in a suitably sized glass vessel placed in a water-bath, and kept at a boil for half an hour. When it is desired to test the orchil by printing, 100 grms. of gum water, 12 of sulphate of alumina, 100 of orchil are mixed and printed by roller or block over a sufficiently large surface of wool, which is afterwards steamed.

Applications of Orchil in Dyeing and Printing.

Orchil is never applied to cotton or calico, for although it might be fixed upon that fibre by means of animal mordants the colours thus obtained are neither sufficiently fast nor brilliant enough to be of any use. This remark does not apply to French purple, which is brilliant as well as fast. In order to print French purple on cotton the lime or alumina lake is dissolved in a mixture of acetic acid and alcohol, next a solution of albumen is added. M. Kopp gives the following prescription, which may, of course, be varied to some extent:—French purple, 25 grms.; acetic acid, 50 grms.; alcohol,

80 grms.; albumen water, I litre; if a bluish hue is desired some neutral indigo extract should be added. The materials are printed, dyed, steamed, and next washed in boiling water.

Cotton as prepared for Turkey-red dyeing (oiled cotton), or also cotton previously albuminised, take up this colouring matter when placed in a bath containing the purple (previously decomposed with its weight of oxalic acid, filtered, to eliminate the oxalate of lime, and next dissolved by the aid of some ammonia); the temperature should be raised to 60°. Non-mordanted wool placed in a boiling hot bath of the ordinary orchil of commerce assumes a beautiful and pure red, violet-red, or violet, according to the quality of the product used. French purple decomposed, or rather deprived of its lime and set free by means of oxalic acid and neutralised with ammonia, yields, upon wool, a very beautiful and fast violet-purple. For the so-called bright groseillered and deep violet-groseille, wool, previously mordanted with tin, is dyed with orchil only, 10 kilos. of wool, 1 kilo. of cream of tartar, 2 litres of tin solution (made up of 400 grms. of common salt, 1.25 kilos. of tin, and 8 litres of nitric acid); the wool is kept for an hour in this mixture at boiling heat. For medium groseille-red ammoniacal cochineal and orchil are used together. Orchil is also used along with other dye-wares to obtain the following colours :-

Amaranth Red.-Mordant for red. Crude cochineal and orchil.

Amaranth Bright.—For medium and deeper hues the quantity of orchil taken is increased, and as regards the very deep hues sulphate of indigo also is added.

Amaranth Violet .- As for preceding.

Feuille Morte.*—The mordanting is done with alum and sulphuric acid (10 kilos. of wool, 2 kilos. of alum, 20 grms. of sulphuric acid, boiled together with water for an hour); the dye material consists of a mixture of orchil, neutral extract of indigo, and turmeric.

Wood Colour (Bois).—Mordanting with cream of tartar and tin solution, dyeing with orchil, neutral extract of indigo, turmeric, and fustic liquor.

The shades known as pommerolle and carmelite are produced by the same mordants and dye-wares, the only difference being the quantities applied. Very large quantities of orchil are consumed in printing woollen fabrics (steam colours). As examples of the shades and of the mode of preparation the following may serve:—Reddish brown (puce) orchil liquor, 2 litres; sulphate of alumina, 120 grms.; senegal gum, 200 grms. Brown (puce) orchil liquor, 2 kilos.; sulphate of alumina, 120 grms.; senegal gum, 200 grms.; indigo carmine, 60 grms. After printing and dyeing the goods are steamed and next washed. In order to apply French purple as steam colour upon wool and silk the dye material is dissolved in acetic acid, neutralised with carbonate of magnesia; alcohol is added, and gum water as thickener; these are applied by cylinder, and the fabric afterwards steamed.

Orchil dyes silk directly without the use of any mordant, the shades being similar to those produced on wool. The French purple yields on silk a beautiful mauve or dahlia colour when used alone. If mixed with indigo extract it yields a very good violet; with cochineal, peach-blossom, groseille,

^{*} A peculiar hue which the leaves of many trees and shrubs assume in the autumn just previous to falling.

and lilac. The material known as litmus is also a product from lichens, and is obtained by a modified process of setting in action the colourable principles contained in them. Litmus is rarely if ever used in dyeing, although it colours silk blue and violet, but the colours produced are so fugitive as to be only employed in extreme fancy styles.

Litmus was chiefly used for washing blues, for colouring wine, vinegar, and cordials, and is still employed by chemists for the preparation of the so-called litmus paper. The ordinary litmus of commerce is made from the Roccella lecanora and variolaria, lichens obtained on the coasts of the Mediterranean. in Sweden, Norway, and the Canary Islands. The raw material is chiefly sent to Holland for conversion into litmus, which is done by adding to the lichens, previously ground to a pulpy mass, a mixture of ammonia and carbonate of potassa (pearl-ash). The paste is left to ferment until a violet colour appears. When this stage is reached lime is added, and also another quantity of pearl-ash and some stale urine, when the mixture is left to ferment for some three weeks longer, until a blue colour is obtained. The pulpy, semi-fluid mass is rendered more solid by the addition of chalk and some plaster-of-paris, the excess of liquor is separated by means of sieves, and after having become sufficiently dry is shaped in jujube or lozenge form, dried either in the open air (in summer) or in heated drying rooms, and delivered to the trade in seven different qualities, No. 1 containing most, and No. 7 least chalk. Litmus so prepared is a dry, light blue substance, the better the quality the less insoluble matter it contains.

The orchil prepared by the action of ammonia upon lichens does not become, when treated with acids, perfectly red, and that colour is not rendered blue by contact with ammonia and alkalies; the presence of carbonate of potassa as used in the manufacture of litmus has therefore the effect of modifying the process of oxidation of the colourable matters, so as to result in the formation of a red acid, which, with alkalies, forms a blue salt. The blue colour of the litmus of commerce is therefore due to the colour of a potassa salt of a red acid. The real colour of that acid is made apparent by the action of stronger acids upon litmus, the aqueous or alcoholic solutions of which all contain an excess of alkali, which has to be saturated first before the colour begins to turn to red.

Since litmus is used as a reagent of some value in chemistry its preparation so as to be most sensitive and delicate for that purpose may not be here out of place: to the litmus solution is added a slight excess of acetic acid; it is next carefully neutralised with ammonia, and then boiled for a long time so as to expel the last traces of any free volatile alkali. All chemists are aware that litmus tinctures when kept in stoppered bottles become gradually discoloured in consequence of a peculiar reductive fermentation, but exposure to the oxygen of the air is sufficient to restore the original colour in full strength. Something similar takes place with orchil; both these substances are similarly affected by the action of reducing agents.

Kane and Gélis have studied the peculiar blue produced from the lichens as present in litmus. The former chemist has found in litmus from three to four distinct colouring matters, which he isolates by the following process:—Litmus is ground to a coarse powder and exhausted with boiling water; the insoluble, pale blue residue is treated with a slight excess of hydrochloric acid, whereby

a red flocculent matter is separated, which, on being collected on a filter, is washed, dried, and next exhausted with boiling alcohol. This solution is evaporated to dryness, and the residue being again treated with alcohol yields a beautiful red semi-fluid substance (erythroleine), soluble in ammonia, with a purplish colour. There is besides dissolved in the alcohol another deep red matter, soluble in ether, and exhibiting a crystalline structure, forming a blue compound with potassa, and with ammonia a blue but insoluble substance (erythrolitmine). There remains after the first-mentioned treatment with alcohol a brownish red, amorphous body, insoluble in alcohol and ether, but soluble in water. It forms with ammonia and the alkalies blue solutions. This is the most important constituent of litmus, being the material which in the state of a blue potassa salt is dissolved in water, when the litmus of commerce is treated with that liquid. The body has been named by Dr. Kane, azolitmine, and contains nitrogen, which is not present in erythroleine and erythrolitmine. According to the author just named, the composition of azolitmine is C7H7NO4, its formation from orcine being according to the following formula: $C_7H_6O_2+NH_3+O_6=C_7H_7NO_4+H_2O$. The action of carbonate of potassa produces a more energetic oxidation of the orcine.

Dr. Gélis first exhausts litmus with boiling water; the residue is boiled with a weak solution of potassa. Both liquids are then mixed and preciptated with subacetate of lead. The precipitate, after having been well washed and suspended in water, is decomposed by sulphuretted hydrogen; the ensuing precipitate of sulphide of lead containing the colouring matter is exhausted with an ammoniacal water. This solution being acted upon by hydrochloric acid yields a flocculent precipitate of colouring matter, a small portion of which remains in solution. This flocculent matter being treated with ether yields a red, somewhat crystalline body, soluble in alkaline liquids, with a violet colour. The residue insoluble in ether, being treated with alcohol, yields a blood-red solution, which, when evaporated to dryness, leaves a purplish red body with a golden reflection, the main coloured constituent of litmus. There remains, moreover, a body insoluble in water, alcohol, and ether, but soluble in alkalies. From this account it is sufficiently clear that the chemical history of litmus is far from complete.

What is known as tournesol en drapeaux, litmus on rags, is almost solely used in Holland to impart to the outer crusts of cheese a red stain, which preserves it to some extent from decay and from the attacks of insects. It is a colouring matter obtained from a kind of euphorbiaceous plant, the Croton tinctorium, purposely cultivated chiefly at Grand-Gallargues, Département du Gard, France. The juice of the fruits, berries, and the young top shoots of this plant is squeezed out, and clean coarse linen or other rags are steeped therein. When dry the rags are hung up in or over vessels partly filled with stale human urine, to which alum and lime have been added, or the rags are simply covered with horse-dung; this operation is locally termed aluminadou. The rags are inspected, and the action of the ammoniacal vapours carefully watched, because excess of that action would destroy the colour. They are next dried, and are steeped a second time in the juice of the plant, but now mixed with urine, after which they are again dried in the sun, and exposed as much as possible to wind. The researches of Dr. Joly,* of Toulouse, have proved that the colouring principle of the

^{*} Joly, " Ann. de Chim. et de Phys." [3], vi., 111.

Croton tinctorium pervades the entire plant at every time of its life, but is chiefly present in the cellular tissue, wherein it occurs as a colourable body. By the action of the oxygen of the air and rapid drying a blue colouration is produced. When the fruit of this plant is immersed in twice its bulk of water and heated to from 50° to 60°, that liquid assumes a rather deep violet-blue colouration, and deposits, on being evaporated, a beautiful azure-blue resinous substance. Acids turn the colour of the aqueous solution to a yellowish red, which is not rendered blue again by alkalies, but becomes greenish. By this reaction, therefore, the "litmus on rags" is distinguished from the litmus of commerce. The researches of Dr. Langdale and Dr. Martius made with the juice of the plant just described have proved that it dyes, without the aid of mordants, a violet-red upon wool, silk, and cotton tissues, and that this colour may be rendered fast by steaming and the simultaneous action of ammonia vapours, which, however, turn the colour more blue. The red colour of the outer crusts of some kinds of Dutch cheese is due to the presence of some lactic and butyric acids in that substance. No good substitute for this "litmus on rags" for the last-named purpose has as yet ever been found. A sum of £10,000 is annually paid by Dutch farmers, chiefly to the inhabitants of Grand-Gallargues, for a commodity which, at first sight, no one would take to be anything else but dirty rags, best suited for paper-making after having been bleached. A portion of the rags, after having being used to rub cheese with, are sent back, because it has been found that the old rags take up and develope the colourable matter far more readily than new ones. The violet-red colour prepared with the various kinds of lichens above mentioned is not the only one which these plants are capable of yielding.

M. Westring has made a series of dyeing experiments* chiefly with lichens growing in Sweden, a country wherein these cryptogamic plants are found in great abundance. Among the varieties he experimented with are:—The Pertusus; sanguinarius, cinereus, rugosus, hamatoma, subcorneus, tartareus, Lichen auritus, centrofugus, saxatilis, parietinus, omphalodes, saxicola, and many others, all found on rocks or the barks of trees. In order to dye with these lichens, M. Westring employs ammonia as the most active solvent, or a mixture of lime (10 parts), with glo of sal-ammoniac upon 1 part of lichen. The addition thereto of a small quantity of common salt is sometimes useful, especially for silk, which thus acquires more lustre. Mordants were not used, as being found to do more harm than good. The colours obtained varied according to the mode of extraction applied, also according to the temperature

and the quality of the water employed.

The colouring matter of some of the lichens can be extracted by steeping them in cold water, and the liquid obtained is immediately suited for the dyebeck; maceration in tepid water extracts the colouring matter from almost all the lichens. The author obtained the following shades upon divers tissues, by more or less varying the treatment above described:—Grey, nut-brown, more or less deep cinnamon, feuille morte, brick-brown, straw-yellow, olive, brown, and violet. Some lichens, among them certain species of *Usnea*, wall lichen, yield to solvents a yellow principle, about which more will be said when the yellow colouring matters are treated.

^{* &}quot;Annales de Chimie," vol. xii., p. 240.

Alkanet.

The tinctorial matter now rarely used, known as alkanet, alkana, or canette, is the root of a plant belonging to the natural order of the Boraginaccæ, called Anchusa tinctoria. It grows wild in Greece, Asia Minor, Italy, and some portions of Southern Germany. The root has been used in pharmacy and perfumery, chiefly as a colouring matter. Its immediate tinctorial principle was first isolated by M. Pelletier, who called it anchusine, or anchusic acid. MM. Bolley and Wydler obtained it in a state of great purity, and called it alkana red. They prepare it by first exhausting the previously dried and sliced root with water, which dissolves and eliminates soluble vegetable principles. The residue is then dried, and treated with alcohol; the violetcoloured alcoholic solution is acidified with hydrochloric acid, and evaporated to dryness. The residue is next treated with ether, which dissolves the colouring matter; the ethereal solution is mixed and well shaken up with water, whereby the colour is obtained in an insoluble state, and is dried after the removal of the fluids by decantation. Dr. Lepage employs sulphide of carbon instead of alcohol, and, after having removed the excess of the formernamed liquid by distillation, he treats the residue with a solution containing 2 per cent of caustic soda, and precipitates with a slight excess of hydrochloric acid. The precipitate is separated by filtration, and, after having been allowed twenty-four hours for settling, is well washed with water, and dried. The material thus obtained is a deep red, brittle, resinous mass, insoluble in water, soluble in alcohol and ether, to both of which it imparts a beautiful reddish-violet colour. An alcoholic tincture of this root is used for colouring the spirit of thermometers. The alcoholic solution is turned blue by alkalies, and yields with bichloride of tin a violet precipitate. The same solution yields with subacetate of lead a greyish-blue, and with acetate of alumina, at a boiling heat, a violet-blue precipitate.

The pure alkana red is not at all affected by boiling its alcoholic solution, but if the alcoholic tincture of the root be evaporated to dryness, without having previously been acidulated with hydrochloric acid, there is a residue left partly soluble in water, and imparting to it a brown colour, while what remains undissolved colours ether greenish. This greenish pigment is, according to Dr. Bolley, formed at the expense of the anchusine, which fixes water and gives off carbonic acid. The precise composition of alkana red is not known. Dr. Bolley states that its formula is $C_{35}H_{40}O_8$, but this is not

proved with certainty to be correct.

Anchusine appears to act as a feeble acid. Its hot alcoholic solution dyes cotton, previously mordanted with alumina, a violet, and when iron mordants are applied a grey. To I litre of alcohol (sp. gr. o.849) 62 grms. of the alkana red are used. The colours obtained are not fast, and are very readily affected even by very weak alkalies and acids.

M. Hausmann, of Mulhouse, introduced the alkana red in calico-printing, but it has never been used to any large extent, and is now altogether obsolete for that purpose. The root and the prepared red are largely used for colouring pomades and hair-oils, as a rouge for the complexion, and as a colouring matter for lozenges.

Safflower.

This substance, also known as wild saffron, is the produce of the Carthamus tinctorius, an annual plant, a native of Southern Asia, and cultivated in India,

also in some parts of Spain, Southern Germany, Italy, Hungary, Persia, China, the Sunda Islands, South America, and Southern Russia. It resembles the thistle: the petals of the plant are, when dried, what is known as safflower, of which the following varieties occur in commerce:—

Egyptian Safflower.—Met with as strongly compressed, somewhat moist, deep red-brown cakes, of a peculiar odour. It is packed in coarse canvas bags, weighing from 320 to 350 kilos. It is cultivated partly near Cairo, partly in Upper Egypt, and is chiefly imported into Trieste, Venice, Leghorn, and Marseilles.

Spanish Safflower.—A pleasant-smelling, deep red, loose mass, very like saffron.

Indian Safflower.—Occurs in commerce in the shape of small, flattened, circular cakes, internally rose-red. It is packed in good canvas, externally covered by wicker-work, the packages weighing from 75 to 150 kilos. Batavia Safflower.—Deep red, well-developed flowers, pressed in bales.

The Egyptian kind is the richest in colouring matter, containing nearly twice as much as that from other countries; yet the Indian and Chinese safflowers are highly esteemed. The goodness of this substance may be judged already by its external appearance, which should be of a fiery red; a dull redness is a proof of bad preparation.

Safflower contains three distinct colouring matters, viz., two yellow principles, one of which is soluble in pure cold water or water slightly acidulated; the other is only soluble in an alkaline liquor: thirdly, a red colouring matter, carthamic acid, the only useful constituent. The quantity of the yellow colour insoluble in water varies in the inverse ratio of that of carthamic (carthamic acid).

According to M. Salvétat, safflower contains—Yellow colour, soluble in water, from 26 to 36 per cent; carthamin, from 0.3 to 0.6 per cent; extractive matter, 3.6 to 6.5 per cent; albumen, from 1.5 to 8.0 per cent; waxy matter, 0.6 to 1.5 per cent; cellulose, 38.4 to 56.0 per cent: further, some pectic compounds and silica, from 1 to 8.4 per cent; oxides of iron and alumina, 0.4 to 1.6 per cent; oxide of manganese, 0.1 to 0.5 per cent.

On treating safflower with cold water, the yellow colouring matter, the salts, and albumen are removed. If the dye ware is treated with water acidulated with acetic acid, filtered, and first acetate of lead and next ammonia is added, the yellow colour is precipitated along with the lead salt. This precipitate is washed, decomposed by means of dilute sulphuric acid, the sulphate of lead separated by filtration, the liquid next evaporated in a retort, preferably in an atmosphere of carbonic acid, but in every case as much as possible with exclusion of air; the residue afterwards treated with alcohol, and this solution evaporated to dryness, yields, on being again treated with water, the yellow colour, which, however, becomes rapidly changed by contact with air. The aqueous solution is acid to test-paper, has a bitter taste, but the yellow matter it contains does not possess any particular interest. Its elimination from the safflower intended to be used as a dye material is of great importance, since the beauty of the colour is impaired by the presence of this yellow matter, especially if animal fibres are to be dyed with the ware.

Carthamin, or carthamic acid, may be prepared in a pure state by making use of its insolubility in water and solubility in alkaline liquids, such as solution

of carbonate, borate or phosphate of soda. For this purpose safflower is first freed, as far as possible, from its yellow colouring matter, by being well washed with acidulated water, and is next treated with a dilute cold solution of carbonate of soda (ordinary washing soda, 15 per cent); the mixture is well squeezed, and to the clear bright yellow liquid thus obtained an acid is added, whereby the carthamic acid, along with many impurities, is precipitated. It would be almost impossible to free the carthamic acid from these foreign substances, but this result is very readily brought about by immersing into the alkaline solution, previous to the addition of an acid, a quantity of cottonwool. This material attracts, by a special action, the carthamic acid at the moment it is set free by the addition of an acid; and the cotton-wool may first be washed in a weak acid, and next in water, and, lastly, again with a weak alkaline liquid, which re-dissolves the carthamin. After removal of the cotton-wool, plenty of which should be used, it is re-precipitated by an acid, very dilute citric or tartaric being the best. It falls down in the state of a beautifully rose-red flocculent matter, which may be collected on a filter, washed, and dried. In order to obtain a still purer material, the flocculent dry substance should be dissolved in alcohol, and this solution, after having been strongly concentrated, is poured into a large bulk of water, and the precipitate thus formed is again collected on a filter and dried. Care should be taken to avoid the use of too strong alkaline solutions,, nor should they be exposed to air for any length of time, since this completely alters the colouring matter.

Carthamin in a pasty state, as obtained by the processes just described, is met with in commerce suspended in water for direct use. The paste is dried upon suitable vessels—porcelain saucers, plates of porcelain, or even upon polished cardboard. The colouring matter, when dry, has a pecular cantharides-like gloss and brilliancy, not unlike fuchsine; the powder is beautifully red, and is used also when mixed with French chalk and rubbed down with

water and again dried, as a rouge.

Carthamin is insoluble in ether, almost so in water, but soluble in alcohol, to which it imparts a cherry-red. This alcoholic tincture dyes silk immediately, no mordant being required. Carthamin is altered by boiling with water and with alcohol; it is soluble in concentrated sulphuric acid, forming a red liquid, but water does not precipitate it from this solution. Nitric acid and dilute sulphuric acid dissolve the carthamin, producing yellow liquids. Carthamin is an acid, the alkaline carthamates being yellow or orange-yellow, and yielding when in solution, on the addition of an acid, precipitates of carthamic acid.

Carthamate of ammonia yields, with bichloride of tin, a yellowish-brown precipitate; with perchloride of iron, a brownish-red; and with bichloride of mercury, a red precipitate.

According to Dr. Schlieper, the composition of the yellow matter of safflower is $C_{16}H_{20}O_{10}$, while the formula of carthamic acid is, according to him, $C_{14}H_{16}O_{14}$.

Before the discovery of the aniline dyes, safflower was very frequently used to dye silk, wool, and even cotton fabrics. In order to apply it to cotton the ware is first placed in canvas bags, and thoroughly washed with slightly acidulated water, so as to eliminate all the yellow colouring matter as much as possible. It is next treated with carbonate of soda (15 per cent of the

crystallised soda of commerce dissolved in water), and in this solution the yarn or fabric to be dyed is immersed; a slight excess of lime-juice is added, to cause the precipitation and adhesion of the carthamin to the cotton. Since silk and wool strongly attract the yellow colour, it is essential to eliminate that substance entirely in order to ensure the full beauty of the safflower shades. For that purpose the method of preparation already described for carthamin is made use of, and the substance precipitated on cotton-wool is frequently submitted to a second purification. Frequently the woollen and silk tissues are first grounded (dyed a first time) with annatto or orchil, previous to the dyeing with safflower.

The goodness and quality of safflower is estimated by a dyeing process with a known weight of cotton: about 4 punces of safflower will dye 1 lb. of cotton cloth light pink; 8 ounces will dye a full rose-pink; and from 12 ounces to 1 lb. will dye it a full crimson. In order to take up this quantity the cotton must be several times dyed in fresh solutions of the colouring matter. No mordant is used for safflower, since none of the mordants known either increase the affinity of the cloth for the colouring matter or give it any greater stability.

The quantity of safflower required to dye silk is nearly the same as for cotton, and the process is precisely similar. There is one peculiarity about the dyeing with safflower which is worthy of special notice: in most other cases the dyer is generally careful to have his dye-wares in a perfectly soluble state for dyeing, but here the exceptional method of precipitating the colouring matter from its solution, before the goods are entered for dyeing, is practised. It is curious to speculate how the coloured particles can be so rapidly and so completely attracted by the fibre as is found to be the case in practice.

The colours safflower yields, although the most beautiful and delicate shades which the art of the dyer can produce, have the disadvantage of being very unstable: nothing is easier than to detect safflower colours upon fabrics; the rose, pink, or crimson hue is at once turned yellow by a single drop of alkali, and is destroyed by any further washing; this property is actually made use of now and then as a discharge, so as to produce a yellow pattern upon a pink ground; weak acids do not affect the colours, but chlorine and sulphurous acid destroy the colour at once.

Practical men generally prefer to extract the red colouring matter from safflower—or, as it is technically called, to bleed it—by several successive applications of the solution of carbonate of soda, using weaker lye at first and stronger ones afterwards. If the resulting liquids are kept separate, it will be found that the first extract yields the brightest and purest colour, whilst the subsequent solutions are progressively inferior. This principle has been taken advantage of in dyeing, the goods being grounded with the last-obtained, or most impure, carthamin, and finally "topped" or finished with the first, or pure, portion of the colour. In this manner an unrivalled "bloom" and brilliance are obtained. The best quality of liquid carthamin, or extract of safflower, may be known by its colour approaching a scarlet. If it be crimson the colouring matter is in a less minute state of division, and the shades produced will be less bright.

The consumption of safflower has been lessened by the introduction of saffranin, which is, in some works on dyeing, designated safflower-substitute.

CHAPTER V.

COLOURING MATTERS OF VARIOUS ORIGIN.

Chica, Crajura, or Carajara.

A PIGMENT used by the Indians in Central America, and which is applied to their bodies mixed with the fat of the alligator. The chica is obtained from the leaves of the Bignonia chica, which the Indians boil for a long time with water, decant the liquid, which contains a reddish-coloured fecula in suspension, and add to the liquid some particles of the bark of a tree known as aryane, which causes the precipitation of the colouring matter. This, when dried, is a vermillion-red, tasteless and inodorous mass, specifically heavier than water; it soils the fingers, and assumes, when rubbed on the nail, a metallic aspect. This substance is decomposed by heat without previous fusion.

Chica is insoluble in water, but boiling alcohol, at 36 per cent, dissolves it. becoming thus ruby-coloured. It is also soluble in ether. The alcoholic solution is not precipitated by water unless heat is simultaneously applied. Alkalies dissolve chica with a vinous-red colour, the solution being precipitated by acids. Caustic potassa, ammonia, and carbonate of potassa dissolve chica, the solutions exhibiting an orange or orange-red colour. centrated acetic and hydrochloric acids also dissolve this substance, yielding a reddish-brown liquid; chlorine turns its original colour to a bright brown; with dilute sulphuric acid it yields, when heated, an orange liquid, from which, on cooling, a granular, orange-red mass is separated, while addition of ammonia causes in the remaining liquid the formation of a deep purplish precipitate. When chica is treated, in a sealed tube, with a mixture of any alkali and glucose, it yields, by reduction, a bluish liquid, which becomes rapidly brown again on exposure to air, and from which hydrochloric acid precipitates an orange-red flocculent matter. Nitric acid attacks chica, converting it into a mixture of picric, oxalic, anisic, and hydrocyanic acids.

According to M. Boussingault, chica—which, he says, contains no nitrogen—dyes cotton a yellowish-orange colour. Dr. Erdmann assigns to chica the formula C₈H₈O₃,—that is to say, it is an isomer of anisic acid.

Chica is rarely met with in Europe, but, from the results of experiments made to ascertain its applicability as a dye, it was found that after treatment with an acid, or with muriate of tin, it would dye very deep shades upon wool; and by treating it with acid, and washing the free acid away, it yields, with mordanted cotton (alumina and tin mordants), shades very similar to those produced by lac-dye. The colours are not so bright as those of

cochineal, but are more permanent, and resist washing and exposure somewhat better.

Colouring Matters Contained in the Sorgho.

Sorgho-Red .- The plant known as "durrha," Sorghum, or Sorgho sacchariferum, -a native of Northern China, and belonging to the family of the Gramineæ, imported into Europe, and cultivated in some portions of Spain, France, and Germany, since the middle of the year 1853, chiefly for the purpose of the extraction of sugar, -contains several colouring matters, among which sorghored or sorgho-carmine, obtainable from the interior of the stems, after the sugar has been removed, by means of the action of dilute sulphuric acid. The pericarpium of the fruits or seeds contains, according to MM. Sicard, I. Itier, and Joulie,* two different red pigments, viz., sorghotin and sorghin, which are employed in China as dye-wares, yielding fast but not very bright colours, somewhat like madder. M. Itier had in his possession pieces of the dyed linen and cotton fabrics which he had seen prepared while in China, and he also had sorgho-red (from the stem of the plant), and sorghotin and sorghin, as sold in some parts of China; but the larger portion of the materials brought by him and his co-travellers to Europe had been deposited with the authorities at Paris, who (the revolution of 1848 intervening) seem to have lost sight of these matters. The cotton dyed with a mixture of sorghotin and sorghin, the cloth having been previously worked about in an emulsion of a peculiar nature, exhibit at first sight no difference from Turkey-red, but it is not so fast,-that is to say, does not stand acids, alkalies, &c., so well as genuine Turkey-red.

Dr. Winter prepares from the stem of the sorgho a red colouring matter, by leaving the stems, deprived of the greatest portion of their juice, to ferment, piled up in heaps, until the colour has become red-brown; the material is then dried, and next cut up to small fragments and treated with water, and afterwards with a weak caustic soda-lye. By this means the colouring matter is dissolved, and, on addition of dilute sulphuric acid, precipitated. The dye thus obtained is a flocculent matter, soluble in alcohol, in weak acids, and in feebly alkaline liquids. By the aid of tin salts, as mordants, this pigment can be fixed upon woollen and silk fabrics, yielding a bright crimson-red colour, tolerably fixed and stable, withstanding light and washing with soap. The use of the sorgho stems as a dye material, after the elimination of the sugar and destruction of the saccharine matter retained in the stems, is in China rather general. There is nothing precisely known as to the nature and origin of the pigment thus applied as a dye. The bark of this kind of sorgho contains a

yellow-coloured matter, xantholein.

Rose-Red, Pink, Red, and Blue Colouring Matters of Flowers.

Although the brilliant colours of flowers are not useful for application industrially, a few words upon these pigments are not out of place.

MM. Fremy and Cloëz infer from their researches that there exist three chief colouring principles in flowers, viz., cyanin, or a blue colouring matter; a rose-red or pink colouring material, in reality the same as cyanin, but

^{*} During the reign of King Louis Philippe these gentlemen were, among some others, sent to China as an industrial and scientific mission, and from some of their reports (never published) portions of this article are made up.

reddened by the acidity of the vegetable juice; and lastly, two yellow principles, viz., xanthin, insoluble in water, and xanthein, soluble therein.

Cyanin is best prepared from the petals of the violet or iris (Florentine), by exhaustion with boiling alcohol, when the petals become decolourised and the liquid assumes a beautiful blue tint. This alcoholic solution turns rapidly to a yellowish-brown, in consequence of a reduction which takes place, but when the liquid is agitated in contact with air the original colour is restored. This reaction cannot be often repeated without causing the destruction of the cyanin. The alcoholic liquid (solution of impure cyanin) is therefore evaporated to dryness on the water-bath, and the residue is taken up with water, which dissolves the blue colour, leaving resinous and fatty matters untouched. The aqueous solution is precipitated by neutral acetate of lead, and the beautiful green precipitate is, after having been well washed with distilled water. decomposed by means of sulphuretted hydrogen; the liquid freed from sulphide of lead by filtration is again evaporated to dryness, the residue taken up with absolute alcohol, and the cyanin precipitated by means of ether. Cyanin thus prepared is a non-crystallisable solid substance, soluble in alcohol and water, insoluble in ether: acids, even if very weak, turn this substance red, while alkalies render it green; reducing agents decolourise it, but oxygen restores the colour.

The red colouring matter of flowers is extracted from the petals by a method similar to that just described, and the material obtained exhibits all the characteristic properties of cyanin.

According to MM. Cloëz and Fremy, the petals of red or rose-red flowers are acid, while those of blue flowers are neutral. Some red flowers assume, while fading, first a blue and next a green colour: this appears to be due to the partial decomposition of a nitrogenous principle, whereby traces of ammonia are set free; other flowers, on the contrary, change from violet to red; a very rapid drying of red, pink, or rose-red flowers, whereby the carbonic acid contained in some of them is eliminated, may cause the colours to become blue. The rose-red, pink, violet, and blue colours of flowers seem therefore due to the same substance, the differences of hues being brought about by a difference in the quality of the vegetable juice. Scarlet flowers, and such as exhibit a high red tint, are assumed to contain cyanin, mixed with yellow matters. Some red flowers, those of the aloe species especially, do not contain cyanin, but instead thereof a peculiar substance, which is hardly soluble in water, insoluble in ether, but soluble in alcohol, and not acted upon, not turned to any other hue of colour, by either acids or bases.

Cyanin appears to be related to the roseo-cyanin formed by the action of boric acid upon curcumin, the colouring principle of turmeric. Both substances are very unstable, and the reactions they exhibit are very similar. The paracarthamin obtained by Dr. Stein, by the action of sodium amalgam upon a mixture of quercetin and meletin, is also in its characters analogous to cyanin.

Colouring Matters of the Malvaceæ.

The petals of the plant known as Althæa rosea, belonging to the natural order Malvaceæ, contain a peculiar colouring matter, soluble in water and alcohol, but insoluble in ether. The aqueous solutions of the petals, freed previously from the calix and stamens, exhibits a violet-red colour, which is turned

crimson by the addition of acids and green by alkalies. The alcoholic tincture of the leaves is purplish-red, and leaves, on evaporation, a deep red residue, free from nitrogenous matter. Cotton mordanted with iron is turned blue or bluish-black by an aqueous infusion of the petals. With an aluminous mordant a violet-blue, and with tin mordants a bluish-violet, is produced. Woollen fabrics, previously mordanted with bichloride of tin, assume a deep violet, and when mordanted with iron a bluish-black or grey; if mordanted with antimonic acid salts, a bluish-violet is obtained: silk mordanted with tinsalts takes a violet.

For calico-printing purposes the alcoholic extract suits better than the aqueous infusion. The colours produced are faster than those yielded by logwood, but they do not stand clearing with soap.

The colouring matter is yet, and was formerly far more so, in great request for the artificial colouration of wines. Latterly it has come into use as a dyeware, and is chiefly so applied in Germany, and more particularly in Bavaria.

Sooranjee, Root of the Morinda citrifolia.

This ware was first imported into Glasgow from India, some years ago: it occurs in pieces of from 2 to 8 centimetres in length, and from 5 to 10 millimetres thick. Externally it is brown, internally yellow; the pigment, or colouring matter, is exclusively concentrated in the bark; its colour is orange-yellow, and it has been named morindin.

The morindin is extracted from the root by exhausting with boiling alcohol: on cooling, the colouring matter is deposited as an impure flocculent material, mixed with a red substance. This crude material is purified by repeated recrystallisation, first from alcohol at 50 per cent, and finally from stronger alcohol acidulated with hydrochloric acid. Thus obtained the substance forms satin-like, needle-shaped, yellow crystals. Morindin is sparingly soluble in cold water, more readily in boiling, but is deposited, on cooling, as a gelatinous mass. It is sparingly soluble in alcohol when cold, but readily when boiling, and best in a weaker spirit; it is insoluble in ether. The aqueous solutions are coloured orange by alkalies; lime and baryta water yield red precipitates, while acetate of lead forms a crimson precipitate: a mixture of a few drops of ammonia added to perchloride of iron causes a brown precipitate in the aqueous solution, while ammoniated alum yields a reddish-yellow precipitate. Morindin dissolves in concentrated sulphuric acid with a deep purple-red colour; the solution, after having been kept for twenty-four hours, yields, on addition of water, a yellow precipitate, insoluble in water, which re-dissolves in ammonia with a violet colouration.

If submitted to the action of heat, morindin first fuses and then enters into ebullition, emitting beautiful orange vapours, which condense to beautiful red needle-shaped crystals, insoluble in water, but soluble in alkaline liquids, with a violet colour. This substance, which Dr. Anderson calls morindon, seems to be the same as that formed under the influence of sulphuric acid. The ammoniacal solution of morindon yields, with alum, a red lake, and gives, upon the addition of baryta water, a blue precipitate. Morindin is dissolved by cold nitric acid, and decomposed by that liquid at boiling temperature.

Prof. Rochleder thinks that morindon is identical with ruberythric acid, and, according to him, morindon is alizarin, but this view is not confirmed by

Dr. Anderson's analysis, which should percentically contain—carbon, 65.81; hydrogen, 4.18: these figures agree very nearly with those which Dr. Schützenberger found for purpurin, viz., carbon, 65.6; hydrogen, 3.2.

According to Dr. Anderson, the colouring matter of sooranjee does not dye fabrics mordanted as usual, but cotton prepared for Turkey-red assumes, when placed in a bath of the ground-up sooranjee, a deep brownish-red colour, very fast, but not at all bright.

The Hindoos have used sooranjee for centuries. They prepare an emulsion of sesam oil and carbonate of soda, steep the tissue therein, dry it in the air, and next steep it in a mixture of sesam oil and pulverised sooranjee root. The fabrics thus take a solid red. We ought to observe that Mr. Bancroft and others, who have examined, in the beginning of this century, a substance also brought from India, and bearing the same name, found no difficulty in dyeing common mordanted cloth with it. The sooranjee is also known to, and used by, the Javanese, and Dr. Rost van Tonningen states that it dyes as well as madder, but the shades are neither so fast nor so brilliant.

Since there is in the India Museum (Whitehall, India Office) a very large number of samples of this substance, which apparently differ, at sight at least, while the Indian names vary, which may arise from the diversity of dialects and languages of Hindostan, there is a field of research open in this direction.

Œnolin, or Red-colouring Matters of Wine.

A few words on the substance just named may find a place here. The subject has been studied by Dr. Glénard,* who obtained the colour from genuine red wine, by precipitation with basic acetate of lead. The blue precipitate is well washed, dried at 100°, put in a displacement apparatus, and while therein treated with anhydrous ether previously impregnated with dry hydrochloric acid gas. The ether which passes through takes up a brown matter, and the precipitate is washed with ether until all acid reaction ceases. The residue of the precipitate, which has a deep red colour, is treated with alcohol (sp. gr. 0.849), which assumes a bright red. This tincture is concentrated by evaporation in a water-bath, and when reduced to a small bulk water is added, which causes the precipitation of a red flocculent substance, insoluble in ether, difficultly soluble in water, soluble in alcohol, insoluble in benzol. When boiled with water for some time this substance turns brown, its composition is changed, and it loses its solubility in alcohol. Hence it is that when wine is evaporated to dryness it gives, when taken up with alcohol, a dirty brownish colour to that fluid.

The weak alcoholic solutions of the pure red colouring matter exhibits the following reactions:—Chlorine destroys the colouring matter, converting it into a yellow substance; potassa solution turns the colour first blue, next brown; lime-water yields a precipitate of dead leaves colour (feuille morte); bicarbonate of soda, a blue colouration; chloride of calcium, a blue colouration; alum turns the colour to light red; with hydrochloric acid, no change; nitric acid converts the substance into a yellow flocculent matter; acetate of lead,

^{* &}quot;Journal de Pharmacie et de Chimie," vol. xxxv., p. 113. "Comptes Rendus de l'Academ, des Sciences," vol. xlvii., p. 268; vol. lviii., p. 268. "Annales de Chimie et de Physique," [3], vol. liv., p. 366. "Répertoire de Chimie Appliquée," vol. iv., p. 328; vol. i., p. 32. "Répertoire de Chimie Pure," vol. ii., p. 306.

blue precipitate; nitrate of lead, violet-red precipitate; acetate of copper, chestnut-brown precipitate.

According to Dr. Glénard the formula of œnolin is $C_{10}H_{10}O_5$. Young wines contain, moreover, according to Dr. Filhol, a peculiar blue colouring matter, soluble in acetic and butyric ethers, yielding bright, beautiful, violetblue solutions, which, by the addition of some ammonia, become first green and next brown. The chemist just named considers that this substance is identical with cyanin as met with in many flowers.

The colouring matter of wine is not industrially employed as a dye, but its properties are of importance, since they may assist in detecting frauds and be useful in medico-forensic researches. Genuine wines are often artificially coloured, but in the wine-growing countries this is done by the addition to the fermenting must of a peculiar kind of grapes, of a very deep blackish-blue colour, purposely cultivated—as, for instance, at Lespane and many other localities—for its colouring qualities.

Among the vegetable colours we notice with a word the following:-

The red cabbage colour, probably cyanin ("Dingler's Polytechnisches Journal," vol. xvi., p. 268): this material becomes green by alkalies, and was formerly in use as a test for them in chemical laboratories.

The red matter of the red poppy flower ("Dingler's Pol. Journ., vol. xxii., p. 271).

The so-called dragon's-blood, a red-coloured resin, the produce of a kind of palm tree, a native of Sumatra and Borneo ("Journal de Pharmacie," vol. xvii., p. 225; "Annalen der Chimie und Pharmacie," vol. xliv., p. 328; "Comptes Rendus," vol. xvii., p. 503; vol. xix., p. 505).

The Lithospermum rose-red ("Répertoire de Chimie Appliquée," vol. i., p. 209; "Archiv. der Pharmacie," vol. cxlvi., p. 278).

The peculiar red of the red cinchona barks.

The bark of the *Lithospermum arvense* yields, when treated with alcohol, a deep red-coloured resinous substance; the alcoholic tincture of deep red colour turns blue upon the addition of alkalies. This resin is soluble in strong sulphuric acid, and exhibits great analogy with anchusin, but is distinguished from it by the colour of its ethereal solution, which is blue, and not red, as is that of anchusin.

Yellow Vegetable Colours.

Of the colours met with in the vegetable world none is so abundant and widely distributed as the yellow, which occurs in almost all plants to a greater or less extent, while the researches of Dr. Thudicum on lutein, of which the following is a brief abstract, prove the identity of some of the yellow colouring matters of the vegetable and animal kingdom:—

By lutein Dr. Thudicum understands a yellow crystalline substance occurring in various parts of animals and plants, as, for instance, the corpora lutea of the ovaries, serum of blood, yolks of eggs, in seeds, as maize (Indian corn), in annatto, in carrots, and the stamens and petals of a great many flowers. Lutein is easily soluble in alcohol, ether, and chloroform, insoluble in water; these solutions are yellow, but that in chloroform, when concentrated, has an orange-red colour. The spectrum of its solutions is distinguished by great brilliancy of the red, yellow, and green part, and by three absorption bands, which are situated in the blue, indigo, and violet part of the spectrum. The

crystals of lutein are apparently rhombic plates, of which two or more are always superposed in a curious manner. The crystals are microscopic, yellow when thin, orange to red when thick, and have no resemblance to any other known animal or vegetable substance. Lutein combines with few substances, mercury-acetate being, perhaps, the only reagent by which it is immediately and completely precipitated as a yellow deposit; mercury-nitrate produces a yellow precipitate which, on standing, becomes white. Nitric acid poured over the crystals produces a blue colour, which immediately passes into yellow. The blue is not produced when nitric acid is added to either the alcoholic, ethereal, or chloroformic solution of lutein, but appears with the acetic acid solution, and disappears again rapidly. Lutein has great affinity for fatty matters and for albumen.

In order to prove further the wide distribution of yellow colours, we quote the names of those vegetable substances which contain a yellow colour in sufficient quantity to make them applicable as dye-wares; these are:—Quercitron bark (from the Quercus tinctoria); true or old fustic (Morus tinctoria, or Broussonetia tinctoria; young fustic, the wood of the Rhus cotinus; the bark, twigs, and berries of the dyer's buckthorn, obtained from various species of the Rhamnus, as for instance, frangula, cathartica, saxatilis, infectoria, oleoides; the Chinese yellow, Gardenia grandiflora; saffron, Crocus sativus; safflower, Carthamus tinctoria; the fruit and leaves of the Bixa orellana (the annatto plant); rhubarb root; wall lichens, Parmelia parietina; weld, the Reseda luteola, entire plant; the root of the Berberis vulgaris; turmeric root (Curcuma tinctoria); the aloe juice; and, lastly, a host of yellow-coloured flowers, some roots, among them the Eschscholtzia, the common carrot, and the mulberry-tree root, and also the shells of various nuts and other vegetable products.

Viewed as a pure immediate principle the yellow pigment obtained from these several plants does not prove to be identical in composition; but it should not be thought, on the other hand, that every species of plant contains a peculiar corresponding colouring matter. It has been proved that many of the yellow pigments obtained from the plants above named are very similar to each other as far as their chemical character is concerned, though their physical properties may differ widely. The yellow colouring matters met with in quercitron bark, Persian berries, fustic, young fustic, weld, and some other plants, are very similar both in their chemical and physical characters; as a result thereof the mode of their practical application and fixation on textile fibres closely corresponds, and the only difference in the shade of the colours produced is the greater or less brightness, a tone verging more or less towards the orange, and the degree of fastness. It will thus render our task easier, both as regards the chemical history of the yellow pigments, and the mode of their application on the large scale, if we include these under the head quercitron yellows.

These yellows as met with in plants are frequently soluble, crystallisable glucosides, which on being boiled with dilute mineral acids are split up into glucose or some analogous substance, and a new body, generally of a deeper colour, and less soluble in water, but very readily so in alcohol, and also crystallisable. This derivative, which while combined with the glucosic molecule is to be considered as the real cause of the colour of the pigment,

may also be met with in free state. Its properties rather differ in different plants; its chemical features are simultaneously those of a weak acid, which can enter into combination with alkalies and metallic oxides, and of a polyatomic alcohol approaching to phenol. The alkaline solutions are orange or brown-coloured, and do not change perceptibly when left in contact with air; heated along with ammonia, contact of air being excluded, an amide is formed remarkable for its ready oxidation in contact with air.

Hlasiwetz has proved that when fusing caustic potassa or sodium amalgam acts upon an alkaline solution of this body it is converted into a saccharine matter and phloroglucin ($C_6H_6O_3$), frequently accompanied by a colourless acid. When sodium amalgam is placed in contact with an acidified alcoholic solution of this substance it is molecularly changed and converted into a red isomeric

principle.

Anhydrous acetic acid heated to 140° with this quercetric yellow converts it into an acetic derivative, the hydrogen of the orginal body being partly replaced by acetyl. The quercetric glucosides or the yellow-coloured body obtained therefrom can only be fixed on textile fibres by the aid of metallic mordants. With hydrate of alumina a yellow shade is obtained, with iron mordants olives, and with oxide of tin yellows or oranges. Quercitron bark is the inner bark of some species of trees belonging to the natural order of Amentaceæ, and botanically known as Quercus nigra, digitata, trifida, and tinctoria. The Quercus nigra, or black oak, so called because the outer epidermis of the bark is black, is a native of the middle and southern states of the U.S. of America. It is a tree attaining a height of from 25 to 30 metres, abundantly met with in the forests of Pennsylvania, Georgia, and Carolina. Quercitron bark, as met with in commerce, is a mixture of fibres and fine powder of a yellow or buff colour. Its preparation is very simple; the bark previously deprived of its black epidermis is ground under millstones, and the fibrous portion (which is the least valuable) is sometimes separated by means of sieves. Three kinds of quercitron are distinguished in commerce, imported from Philadelphia, New York, and Baltimore, the first being generally preferred.

The celebrated Bancroft was the first to apply (1775) this now highly appreciated dye-ware. The decoction of quercitron exhibits an orange-yellow colour. If exposed to air it very slowly deposits its colouring matter (quercitrin or quercin) in a crystalline state. After standing for a long time thus exposed the colour turns brownish red, and at last it becomes a thick clotted mass. Its properties are: odour of the oak bark decoction, like that of freshly charged tan pits; taste, bitter astringent; reaction, acid to test-paper; the addition of alkalies and alkaline earths deepens the colour of the decoction, the latter simultaneously producing a reddish flocculent precipitate. With the undermentioned substances the decoction of quercitron yields the following reactions:—

Alum, a very slight precipitate; proto and bichloride of tin, acetate of lead, acetate of copper, chloride of barium, nitrate of silver, yield yellow precipitates verging upon red or olive; salts of iron, a green colouration and olive precipitate; mineral acids render the colour of the decoction brighter, and produce a flocculent precipitate; acetic acid merely brightens the colour; solution of gelatin gives a flocculent precipitate. The more interesting immediate

principles of this decoction are—(1) a peculiar tannic acid, called quercitannic acid, which colours the iron salts like ordinary tannic acid, but does not, like that acid, yield gallic acid; (2) the quercitrin or active principle.

In order to estimate the tinctorial value of quercitron (or, as it is commonly called by dyers, "bark") a piece of previously mordanted cotton is dyed with the ware to be tested, the operation being conducted as described under madder, and the results compared with those obtained simultaneously with a sample of quercitron known to be of good quality. A pale yellow colour of the quercitron may be taken as an indication of good quality. A few grammes of the sample may be burned off in a platinum crucible as a test for mineral adulterations, while the moisture also should be estimated by drying the sample at 120°.

Colouring Matters Contained in Quercitron.

I part of quercitron boiled for a quarter of an hour with 10 parts of water deposits, after some days' standing, a crystalline body, named quercitrin by M. Chevreul.* Dr. Bolley describes this principle as quercitric acid, and prepares it by exhausting the quercitron of commerce in a displacement apparatus with alcohol at 84 per cent. The tannin (ordinary tannic acid) contained in the solution is first removed by gelatin, and after filtration the solution is evaporated to dryness, yielding a crystalline mass, which is purified by several re-crystallisations from alcohol.† Some varieties of quercitron contain a substance soluble in cold water, and capable of being split up at 60°, in

the presence of water, into sugar and quercitrin.

M. E. Schlumberger once accidentally when working upon such quercitron succeeded in extracting quercitrin therefrom with the greatest ease by simply heating to 60° the cold aqueous infusion of the bark. The liquid when so heated became turbid, and deposited the quercitrin in beautiful mother-of-pearl-like shining crystals, which were nearly chemically pure. It rarely happens that this phenomenon can be reproduced with the bark as imported; probably the result would be more satisfactory with the fresh bark, since it is not unlikely that the material known as flavin, and manufactured in the United States, although chiefly consisting of quercitrin, is produced by a similar process to that employed by M. Schlumberger. Any chemist desirous to prepare quercitrin in quantity will do best to operate on flavin. It is only necessary to boil it with a large quantity of water, and to filter while boiling hot; the liquid on cooling deposits quercitrin in a crystalline state, and almost perfectly pure. Quercitrin is hardly soluble in cold water, but 25 parts of boiling water dissolve it; it is also soluble in alcohol, but not well in ether. Ammonia and the aqueous solutions of caustic alkalies dissolve quercitrin readily, the colour of the solutions being a greenish yellow. The ammoniacal solution is rapidly oxidised by the action of air, and turns brown. Baryta water causes in the aqueous solution of quercitrin a reddish yellow precipitate; with alum solution a beautiful yellow colour is produced; the acetates of lead and copper and the chloride of tin yield flocculent yellow precipitates; persulphate of iron turns the colour olive-green, and causes a

^{*}Chevreul, "Leçons de Chimie Appliquée à la Teinture," a valuable and now very rare book; for years out of print.

Bolley, "Annalen der Chemie und Pharmacie," xxxvii., 101.

gradual precipitation. Nitric acid colours quercitrin orange-red, and concentrated sulphuric acid dissolves it. Quercitrin is a bright yellow crystalline, inodorous powder, of a somewhat bitter taste and feebly acid reaction. Under the lens the powder appears as small rectangular tubular crystals. As obtained by the cooling of an aqueous solution quercitrin has the appearance of a mother-of-pearl-like shining bright yellow substance. When submitted to heat it yields a yellow sublimate, and leaves an abundant residue of charcoal. There exists some uncertainty as regards the proper formula of quercitrin; several which have been proposed agree each with the results of the elementary organic analysis, but since certain experimenters have overlooked what was proved by Dr. Hlasiwetz, that quercitrin does not become completely anhydrous below 200°, retaining a part of its water of crystallisation nearly to that temperature, it is conceivable that there exist discrepancies in the centesimal results of the elementary analysis. Quercitrin is a glucoside capable of being split up into a kind of sugar, and a yellow principle, "quercetin;" the formula to be assigned to quercitrin will therefore to a certain extent, and within the limits of a more exact chemical analysis. depend upon the formula of quercetin, and since we cannot discuss the constitution of the latter as yet, we give here the centesimal results of those analyses of quercitrin which appear most correct:-

Dried at 200°				
MM. Zwenger and Drouke.	MM. Hlasiwetz and Pfaundler.	Incompletely dried.		ried.
Carbon 56.0	56.2	55.7	54.1	52.4
Hydrogen 4.6	4.2	5.5	5.5	4.9

According to the researches of M. Rigaud,* an aqueous solution of quercitrin acidified with sulphuric acid and boiled becomes turbid, and deposits even while yet hot an abundance of a flocculent material far more deeply yellow than quercitrin, and nearly insoluble in boiling hot water. This phenomenon is best seen by heating together pure quercitrin and water, to which one-tenth of sulphuric acid is added; at a moment when the temperature is sufficiently high the quercitrin becomes dissolved, and a moment after the liquid turns suddenly intensely yellow, next turbid, and then deposits flakes of quercetin. The liquid from which the quercetin has been separated by filtration is first treated with carbonate of baryta to eliminate the sulphuric acid, and is, after filtration, evaporated, thus yielding a syrup, which, according to Zamminer, may become a crystalline mass. The sugar is not possessed of rotatory power; it reduces alkaline solutions of salts of copper, and its composition corresponds to glucose $(C_6H_{12}O_6)$.

Hlasiwetz and Pfaundler have come to other results; the evaporation of the syrup yielded them after a few hours a beautiful crystalline substance, which crystallographically agrees with saccharose or cane-sugar; these crystals dissolve at 18° in 2·09 parts of water, and also in absolute alcohol; they taste sweeter than glucose, and deflect the plane of polarisation to the right (specific deviatory power=0·0763°). This sugar is incapable of fermentation, and its formula is $C_6H_{12}O_5+H_2O$. The last molecule of water may be eliminated at 110°; it reduces the cupreous test liquor, and fuses at 107°. If treated with a mixture of concentrated nitric and sulphuric acids, the sugar just

^{* &}quot;Annalen der Chemie und Pharmacie," xc., 283.

mentioned yields a body, $C_6(NO_2)_3 \\ H_9 \\ O_5$. This sugar is isomeric with mannite and dulcite, and has been named isodulcite.

Hlasiwetz and Pfaundler state that there exist various kinds of quercitrin, which differ by the nature of sugar in combination, while the composition of the other constituent, the quercetin, is constantly the same. Quercetin, first discovered by M. Rigaud as the product of the splitting up of the quercitrin, is, according to Dr. Bolley, also found either isolated or in a glucose combination in other plants.* He states that Persian berries yield, when treated with ether a yellow colouring matter, which, on being purified, first by the evaporation of the ether, next precipitated by water, then taken up by alcohol, and slow evaporation of this solution after addition of water, yields a substance exhibiting all the characters as well as the composition of quercetin.

Schützenberger and Berlèchi state in reference to this assertion of Bolley, that a full investigation of rhamnetin, obtained by the splitting up by means of sulphuric acid of the rhamnin (the coloured glucoside of the Persian berries), has proved that rhamnetin, however much resembling quercetin, cannot be confounded therewith, and the question therefore is, whether the substance taken for quercetin by Dr. Bolley is not in reality rhamnetin.

Rochleder and Hlasiwetz have extracted quercetin from the flower-buds of the Capparis spinosa, and Stein has found it in the immature flower-buds of the Sophora japonica. Rochleder has proved the existence of quercetin in the bloom and ripe fruits of the horse-chestnut (Æsculus hippocastanum).† The yellow pigment found by Dr. E. Schunck in the leaves and stems of the buckwheet plant (Polygonum fagopyrum), is identical with rutin. According to Bolley and Mylius, the yellow pigments of fustic ought to be considered as quercetin. Hlasiwetz thinks that thuyin of Kawalier does not differ from quercitrin, while the meletin obtained by Stein by splitting up melin also appears to be quercetin. The robinin obtained by Zwenger and Drouke from acacia flowers (Robinia pseudo-acacia) differs from quercetrin, but may be like that substance split up into sugar and quercetin. § Robinin is also found in the flowers of the Carvus mascula. These instances are quoted here to prove the wide distribution of quercetin and its glucosides throughout the vegetable kingdom. When pure, quercetin is a lemon-yellow, crystalline powder, of a far richer shade than quercitrin. It is tasteless and colourless, insoluble in cold, and nearly so in boiling, water, and it is thereby distinguished from rhamnetin, which deposits from a litre of its boiling solution a weight of 0.653 grm. on cooling, while the quantity of quercetin so deposited is quite insignificant. Quercetin is very soluble in alcohol, and cannot be readily obtained from such a solution in a crystalline state, except by the addition of water.

Quercetin is readily dissolved by boiling acetic acid and solutions of alkalies, the liquor in the latter case having an orange-yellow tint; acids precipitate

^{* &}quot; Annalen der Chemie und Pharmacie," cxv., 54.

^{+&}quot;Chemisches Centralblatt," new series, iv., 162. "Comptes Rendus de l'Académie de Vienne," xxxiii., 365.

^{\$} Schweitzerische, "Polytechnische Zeitschrift," ix., p. 22.

[&]quot; Comptes Rendus de l'Académie de Vienne," xxix., p. 10.

^{§ &}quot;Ann. der Chem. und Pharmacie," supplementary vol. i., 257.

^{¶ &}quot;Journal für Prakt. Chem." lxxxviii., 280.

the quercetin from these solutions unaltered. The ammoniacal solution of quercetin becomes brown in contact with air; the alcoholic solution yields, with lime and baryta waters and solution of acetate of lead, orange precipitates. Quercetin yields with chloride of tin an orange colour, and a green with perchloride of iron. When quercetin, suspended in water, is submitted to the action of chlorine it becomes oxidised and dissolves; the dry quercetin yields, under the influence of chlorine, an orange matter, probably a substitution product; nitric acid, fuming and common, attacks quercetin, red fumes being given off. The alcoholic solution of quercetin is decolourised and reduced by nascent hydrogen; when acted upon by concentrated sulphuric—or, better yet, fuming sulphuric—acid, quercetin is dissolved, giving rise to the formation of a yellow sulpho-acid, soluble in water, of an acid taste, and capable of directly dyeing woollen tissues yellow without the aid of a mordant.

Quercetin is not even decomposed by a temperature of 350° C., and at higher temperatures is destroyed without any volatilisation. It retains its water of crystallisation most tenaciously; 100 parts of air-dried quercetin lose, at 120°, 11.5 parts of water, but it requires a temperature of 200° to eliminate the last traces. Quercetin, dried at that temperature and analysed, yielded, according to Hlasiwetz and Stein, centesimally-Carbon, 600 and 60.3; hydrogen, 3.7 and 3.9. Guided by his experiments on the splitting up of quercetin into phloroglucin (C₆H₆O₃) and into quercetic acid (C₁₅H₁₀O₂), he assigns to quercetin the formula $C_{27}H_{18}O_{12}$ (centesimally = C, 60.7; H, 3.4). Schützenberger and Bertèche have proposed for quercetin the formula C11H8O5, as better agreeing with the results of the analysis (centesimally = C, 60.0; H, 3.8), and that formula makes quercetin the lower homologue of rhamnetin (C₁₂H₁₀O₅). While heating quercetin with anhydrous acetic acid (C₆H₄O₃) the two last-named chemists obtained a crystalline acetic derivative, of the formula C11H8O5, containing 3 or 4 atoms of acetyl (C2H3O) substituted for 3 or 4 atoms of hydrogen.

Quercetin can combine with potassa, soda, and oxide of zinc: a hot and concentrated solution of r part of quercetin and 3 parts of carbonate of potassa deposits, on cooling, fine needle-shaped crystals, very readily changeable, which may be dried between folds of blotting-paper, but cannot be again redissolved in water without undergoing decomposition, unless carbonate of potassa be added. The crystals are even somewhat altered by drying in the air at common temperatures. When 5 parts of carbonate of soda and 1 part of quercetin are taken, the corresponding soda compound is obtained. According to Hlasiwetz the formulæ of these compounds are— $C_{27}H_{18}O_{12}K_2O$; $C_{27}H_{18}O_{12}Na_2O$. Dr. Schützenberger prefers the formulæ $C_{11}H_7KO_5$ and $C_{11}H_7NaO_5$.

Hlasiwetz and Pfaundler found, on thoroughly investigating the action of caustic potassa upon quercetin, the production of three substances, viz. phloroglucin, quercetic acid, and paradatiscetin, obtained by adding to a solution of 3 parts of potassa in 1 part of water put into a silver dish, 1 part of quercetin, and rapidly evaporating that mixture to dryness. In order to separate these bodies the alkaline mass is first dissolved in water, and next neutralised with hydrochloric acid. By this operation the first two bodies remain in solution, but the paradatiscetin, still mixed with some quercetin, is precipitated in an impure state; the liquid is next filtered, and, after the

addition thereto of the quarter of its bulk of alcohol, is repeatedly shaken up with ether, which dissolves phloroglucin and quercetic acid. The liquids having been allowed to settle, the upper layer (ether) is decanted off and evaporated to dryness, the residue is taken up with water, and the solution precipitated with basic acetate of lead. The filtrate yields, after treatment with sulphuretted hydrogen, to eliminate the lead, and removal of the sulphide of that metal, on concentration, crystals of phloroglucin, C6H6O3, a kind of saccharine matter related to orcin, and also discovered by Hlasiwetz among the products of decomposition of phloretin. The plumbic precipitate is first washed, next suspended in water, and decomposed by a current of sulphuretted hydrogen, and the resulting liquid, after filtering off the lead compound, is concentrated either by evaporation in vacuo or by gentle heat in a current of hydrogen gas. The crystalline matter obtained is purified by re-crystallisation and decolouration over animal charcoal. The silky-looking needle-shaped crystals thus obtained are quercetic acid,—a weak acid, hardly soluble in cold water, soluble in boiling water, alcohol, and ether; the acid slightly reddens blue litmus-paper, and has an astringent taste; it reduces nitrate of silver, and imparts to perchloride of iron a blue colour, while the acid assumes in the presence of alkalies a magnificent purple-red. Sulphuric acid dissolves quercetic acid, yielding a red-brown solution, from which water precipitates a red flocculent matter, soluble in alkalies with a purple colour. The formula of quercetic acid is, according to Hlasiwetz, C15H10O7.

Paradatiscetin precipitated from the potassic solution by hydrochloric acid is purified by being first washed with boiling water, next dissolved in strong alcohol, and precipitated by acetate of lead, whereby the unaltered quercetin is removed. The lead from the filtrate is removed by sulphuric acid, and the liquid, after filtration, concentrated by evaporation to one-third its bulk. This stage having been reached, the addition of water causes the precipitation of a bulky, white, flocculent mass, which, when re-dissolved in boiling hot but very dilute alcohol, yields, on cooling, shiny yellowish needle-shaped crystals. This substance is an acid, yielding with bases-and especially baryta and strontia-well-crystallised compounds. Paradatiscetin, the acid named, is very sparingly soluble in cold or boiling water, but readily soluble in weak alcohol; less soluble in ether. Its alcoholic solution is coloured an intense deep purple by the addition of perchloride of iron; acetate of lead does not precipitate the alcoholic solution, but yields with the aqueous solution a yellow precipitate; weak caustic potassa and soda dissolve paradatiscetin, the liquid at first appearing yellow, but soon turning grass green on contact with air; addition of an aqueous solution of bromine colours the aqueous or alcoholic solution first red, and next brilliant violet; addition of an alkali to this liquid turns the mixture blue; and if next hydrochloric acid be added, there ensues a red flocculent precipitate, which yields with alcohol a red solution. Chlorine water causes a brown-red colouration, while the solution of paradatiscetin is coloured reddish-brown by solution of bleaching-powder.

When submitted to heat, paradatiscetin fuses, yielding a reddish-yellow mass. The composition of this substance is—

$$C_{15}H_{10}O_6 = \underbrace{C_{15}H_{10}O_7 - O}_{Quercetic \ acid.}$$

The baryta salt, 2C₁₅H₁₀O₆,Ba,H₂O₂, crystallises in needle shaped crystals.

The formula $C_{15}H_{10}O_6$ is also given by Dr. Stenhouse to datiscetin, a body extracted by him from *Datisca cannabina*. It appears that the properties of this latter body and of paradatiscetin agree so closely as to allow the conclusion that these substances are identical. When the reaction of caustic potassa with quercetin is pushed further, the first-named substance is split up into two new substances, viz., quercimeric and protocatechuic acids; the former is very soluble in water, alcohol, and ether, crystallises in granular masses, and is coloured a deep blue by perchloride of iron; its reactions are rather similar to those exhibited by quercetic acid. Its formula is $C_9H_6O_5+H_2O$.

Protocatechuic acid, $C_7H_6O_4$, is soluble in ether; it takes a greenish-blue colour with the salts of peroxide of iron: addition of alkaline carbonates turns this colour to a red. Neutral solutions of protoxide of iron (neutralised by means of carbonate of baryta) yield, with protocatechuic acid, a beautiful violet colouration.

When a sodic solution of quercetin is heated with sodium amalgam until the deep brown first produced has become brownish-yellow, and the mixture is next neutralised with hydrochloric acid, air being excluded, and the liquid shaken up with ether, phloroglucin and two other substances are isolated, one of which, $C_7H_8O_3$, is very soluble; the other, insoluble but readily crystallised, is $C_{13}H_{12}O_3$. An alcoholic solution of quercetin, acidulated with hydrochloric acid, assumes, when in contact with sodium amalgam, a purple colour, and the liquid yields, on concentration, red crystals analogous to isomorin. This material kept in alcoholic solution reproduces quercetin very readily, especially if an alkali be present. Dr. Stein* first described this substance as paracarthamin: it becomes yellow under the influence of alkalies, but acids restore the red colour; it differs from carthamin only by containing more water.

Hlasiwetz and Pfaundler have fully described and illustrated, by a series of formulæ, all the reactions and the results thereof relating to quercitrin and its various derivatives, but as yet the precise molecular weight of quercitrin and quercetin are not established.

Use made of Quercitron.

Quercitron is met with in trade as a powder, and is also used in that state in dyeing. Relying upon the labours of M. Rigaud, and upon the splitting up of quercitrin into glucose and quercetin, M. Leeshing commenced, in 1855, to boil the quercitron with dilute sulphuric acid: if this operation is succeeded by a thorough washing of the material with cold water, the result is the removal of the tannin and lime-salts from the ware, and the conversion of the soluble quercitrin into sparingly soluble quercetin. Leeshing boils for an hour, by means of a jet of steam, in a leaden tank supported by strong woodwork, 80 gallons of water, 100 kilos. of concentrated sulphuric or 200 kilos. of hydrochloric (sp. gr. 1192), and 200 kilos. of quercitron: after standing the acid liquid is decanted, and the residue thoroughly washed with cold water, first by decantation and next on cloth filters, and the mass (purified quercitron) is finally strongly pressed.

Another plan is to boil 500 kilos. of quercitron with a solution of 15 kilos.

^{* &}quot;Zeitschrift für Chemie und Pharmacie," 1863, p. 467. "Journal für Prakt. Chemie," vol. lxxxv., p. 351, and vol. lxxxix., p. 491.

of crystals of soda (carbonate), in 4000 kilos. of water, for a quarter of an hour, and next 61 kilos. of concentrated sulphuric acid are added, and the mixture boiled for three-quarters of an hour, and afterwards washed and pressed.

M. G. Schæffer boils 100 parts of pulverised quercitron with 280 parts of

water and 25 parts of concentrated sulphuric acid.

M. Schlumberger prefers 100 parts of quercitron, 300 of water, and 15 of acid: 100 parts of quercitron yield 85 parts of what is termed "commercial quercetin," which has as much tinctorial value as 250 parts of quercitron.*

This material (viz., the commercial quercetin) possesses the following advantages over the quercitron:—(1). The removal of the tannin contained in the quercitron, whereby the injurious action of that tannin upon the brightness of the colour is prevented. (2). An absolute gain as to colouring matter is obtained. (3). The shades produced on the textile fabrics are more full-bodied and livelier. On the other hand, dyeing with this preparation requires a higher temperature (100°) than quercitron; the portions intended to be kept white are more soiled; the shades produced are more fugitive; and, lastly, owing to the insolubility, or at least sparing solubility, of the quercetin, no decoctions of the commercial quercetin can be made. M. Schlumberger has found, however, that boiling with dilute sulphuric acid, applied to other yellow colouring matters,-as, for instance, sumach, weld, Persian berries, fustic, turmeric,-yields excellent results, as far as the brightness of the colours produced and the productivity of the ware are concerned; so that, just as in case of quercitron, there are obtained, by the above treatment, preparations of absolutely increased tinctorial value.

The most important commercial preparation of quercitron is flavin, a dyeware about which there is no little mystery, -due, perhaps, to the fact that the name has been given to a variety of bodies obtained by totally different processes. English made flavin is obtained by dissolving out the colour of quercitron in weak alkaline solutions, and precipitating by the addition of sulphuric or hydrochloric acid. It is sometimes adulterated with common salt to the extent of 8 per cent. There are again flavins so-called, imported from America, which appear to be merely bark, mechanically purified by a process of thrashing and sifting. The superior American flavin is said to be made by cutting up the perfectly fresh bark, freed from its epidermis, and extracting it with steam at a temperature of 102° to 103° C. The condensed water contains the flavin partly in solution and partly in suspension. Several patents for the manufacture of flavin have been taken out in the United States. Some flavins, on chemical examination, prove to be nearly pure quercitrin, and others nearly pure quercetin, a fact which proves want of uniformity in the mode of preparation. Good flavin has about sixteen times the tinctorial value of quercitron bark.

For the purposes of calico-printing either the freshly-prepared decoctions of quercitron are used, or liquid extracts of a specific gravity varying from 1.070 to 1.152, and known as bark liquor, or the substance known as flavin, and imported from America in the form of an olive-yellow powder.

Quercitron and its commercial derivatives yield, to mordanted calico, the undermentioned shades:—With aluminous mordants, canary-yellow; with

^{* &}quot;Bulletin de la Société Industrielle de Mulhouse," vol. xxvii., p. 411.

iron mordants, grey, olive-green, and a peculiar kind of black, according to the strength of the mordant applied; with oxide of chromium, an olive-yellow; with a mixture of alumina and iron, reseda-colour is produced (the colour exhibited by the flower known as Reseda or mignonette); with tin mordants a yellow is obtained.

Persian berries—often simply known as "berries," or with a series of additional aliases, chiefly indicating the country whence they are imported—are the seed-bearing fruit of different species of shrubs known as Rhamnus, and growing wild or cultivated in Southern France, in Spain, Italy, Turkey, Roumania (the Moldo-Wallachian States), the Levant, and Persia. The berry has the size of a pea, but bears three or four semicircular depressions, corresponding to the number of the flattened seeds it contains. The colour of the dried ware, as met with in commerce, varies from yellowish-green to black, but berries of the latter colour are too old to yield any good results in dyeing. The taste of the berries is bitter, and they give off a very nauseous and sickening smell. The following kinds are met with in the trade:—

- The Persian berry properly so-called is larger than the other kinds, and produced by the Rhamnus amygdalinus, oleoides, and saxatilis. It is imported from Smyrna and Aleppo: the colour is beautifully green; shape elongated; size that of a large pea, four seeds triangular-shaped; taste bitter; very rich in colouring matter; sorted, according to size, in three varieties—large, middling, and small.
- 2. Levant berries, grown in Natolia and other parts of Turkey; brought to Europe by way of Constantinople and Smyrna. Their size is that of a peppercorn; they contain three seeds. Among the best kinds of the socalled Levant berries are those grown in Roumania and Bessarabia.
- 3. Morea berries. A large-sized berry, containing two seeds; colour a light yellow.
- 4. Avignon or French berries; the produce of the Rhamnus infectorius and alaternus. Colour deep green; size of a peppercorn; shape flattened, contains two seeds; quality less good than the Persian.
- Spanish berries; the produce of the Rhamnus saxatilis. In shape and size like to the previous-named kind; colour rather more yellow, and considered of better quality.
- Italian berries; the product also of the Rhamnus infectorius, and very similar to the Avignon berries.
- 7. Hungarian berries; the product of the Rhamnus catharticus and saxatilis.

 The size of peas; are considered of good quality.

The decoction of these berries has a yellow-greenish colour, and turns orange on the addition of alkalies or alkaline earth, which latter also cause the formation of a slight flocculent precipitate. The decoction is not precipitated by acetate of lead or acetate of copper; tin-salt turns the colour of the decoction to a greenish-yellow.

The colouring matters known as xanthorhamnin, rhamnin, chrysorhamnin, rhamnetin, and rhamnoxanthin, contained in the berries just mentioned, now require our attention. The berries contain several colouring glucosides soluble in water, and besides, according to Bolley, a yellow colour insoluble in water, which he states to be quercetin. The existence of several

colouring glucosides in these berries appears proved by the labours of Persoz,* Gellaty,+ Ortlieb,‡ Schützenberger and Bertèche.||

M. Persoz observes, that when decocions of the berries are left for a length of time to themselves they enter into alcoholic fermentation, thereby depositing a crystalline matter, sparingly soluble in water. This appears due to a slow saponification of one of the glucosides. M. Ortlieb found that when a decoction of the berries is acidulated with sulphuric acid, and then boiled, the same reaction is effected in a few minutes. M. Gellaty has extracted from the berries, by means of alcohol, a large quantity of a yellow, crystalline, insipid matter, soluble in cold water and alcohol, but not in ether, and capable of being split up, by means of ebullition with dilute sulphuric acid, into glucose and another yellow flocculent body. The first-mentioned body he calls xanthorhamnin, and the derivative rhamnetin, and represents this reaction by the following formulæ:—

 $\underbrace{C_{23}H_{28}O_{14} + 3H_2O}_{\text{Xanthorhamnin.}} = \underbrace{C_{12}H_{24}O_{12} + C_{11}H_{10}O_5}_{\text{Rhamnetin.}}.$

The substance obtained by M. Ortlieb while boiling a decoction of the berries with dilute sulphuric acid, and that investigated by Dr. Schützenberger and M. Bertèche, are evidently also rhamnetin, which latter, when properly purified by means of dilute alcohol and ether, is a crystalline golden-yellow body, sparingly soluble, even in boiling water (τ litre of boiling water dissolves 653 milligrammes). What is dissolved is precipitated on cooling. The substance is easily soluble in alcohol and ether. The last-named chemist found that the results of the elementary analysis of this substance agreed with the formula $C_{12}H_{10}O_5$.

When rhamnetin is heated along with caustic potassa it is, like quercetin under the same conditions, split up into a saccharine matter and an acid, the composition of which was not determined. If heated to 140°, in sealed tubes, with anhydrous acetic acid, rhamnetin is converted into several acetic derivatives, insoluble in water, of a pale yellow colour, and among which one is found capable of separating from an alcoholic solution in white crystals. Rhamnetin may therefore be viewed as a polyatomic alcohol; and it would appear probable that, if the formula of quercetin is taken at C₁₁H₈O₅, it is a lower homologue of rhamnetin, but even if the identity of the two bodies just named were positively settled, which is not the case, there is no possibility of confusing quercitrin and xanthorhamnin, the latter being far more soluble in water than the former.

Judging by its properties and composition, the substance extracted by Dr. Kane from yellow berries, by means of ether, and named by him chrysorhamnin, appears to be rhamnetin, and the same remark applies to the body which M. Fleury named rhamnin, and which he obtained from the young twigs of the Rhamnus shrub. The rhamnoxanthin, which Buchner obtained from the bark and berries of a shrub related to the Rhamnus species, appears to differ from rhamnetin by being volatile.

- * "Traité de l'Impression des Tissus," vol. i.
- + " Edinb. New Phil. Journal," vol. vii., p. 252.
- ‡ "Bulletins de la Sociéte Industrielle de Mulhouse," vol. xxx., p. 16.
- || Ibid., vol. xxxv., p. 455.
- § "Journ. de Pharm.," vol. xxvii., p. 666.
- ¶ Ibid., 3rd series, vol. xxiv., p. 50.

The colouring matter contained in the berries produces, upon mordanted cloth, colours analogous to those mentioned under quercitron; the yellow is brighter and more intense, but also more fugitive. In dyeing, as well as in printing, the berries-either whole or previously bruised-are employed, or decoctions more or less concentrated. When the berries are exhausted with boiling water, the first decoctions are of better quality, and yield purer colours than the second and third: the decoctions should be used when freshly made, because they spoil and turn "greasy" as it is termed. The berries are also applied in woollen dveing, and for the colour known as stil de grain-a kind of vellow lake—used as paint, especially for in-door work and theatrical decorations, and prepared by precipitating with milk of chalk a decoction of the berries mixed with alum, either alone or with the addition of quercitron and fustic, and by gently drying the precipitate thus produced. The chief use of the berry-liquor is for steam- and so-called application-colours. The decoction is often made with water and vinegar, as producing a liquor which keeps better. The chief use of this yellow pigment is in greens.

Fustic, Yellow Brazil Wood, Cuba Wood, Yellow Wood, Old Fustic.

Under the above names there is imported, from different tropical regions, the decorticated wood of a tree botanically known as Morus tinctoria, belonging to the natural order of the Urticaceæ, and growing wild in some portions of India, the hotter part of South America, Mexico, Jamaica, Cuba, Tobago, often attaining a height of 20 metres. The wood is found in large pieces, sawn straight at both ends, but otherwise rather of irregular shape, and deprived of its bark. The wood is hard, but brittle and light; its colour is a pale lemon-vellow.

The trade distinguishes several varieties, according to the locality of exportation, which is not always identical with the locality of growth. Among these varieties we notice—Cuba wood, considered the best; Tampico, generally a little brighter-coloured than the preceding; yellow Brazil wood, colour very bright, and usually more or less attacked by worms; further, Porto Rico, Carthagena, Macaraïbo, St. Domingo, Jamaica, Tuspan, and India woods. The higher qualities are the hardest and also the least worm-eaten, of a light yellow colour, with reddish veins. This wood is often sold ground-up or reduced to shavings.

The decoctions have the following behaviour with different reagents:—Alkalies and alkaline earths, deep orange-yellow colouration, without any precipitate: sulphuric, nitric, and oxalic acids produce a slight precipitate; alum, a yellow precipitate; sulphate of peroxide of iron, first an olive colouration, next a deep olive-black precipitate;* chloride of tin, acetate of lead, and acetate of copper produce a yellow or brownish-yellow precipitate; gelatin gives a yellow flocculent precipitate.

The colouring matters contained in this wood have been investigated by Chevreul, Wagner, and, more recently, by Hlasiwetz and Pfaundler. These

^{*} The idea of olive-black may perhaps seem preposterous to those of our readers who never saw that fruit fully ripe, but in that state its colour is indeed deep greenish-black, with a bronze reflection.

^{+ &}quot; Leçons de Chimie Appliquée à la Teinture," vol. ii., p. 150.

^{‡ &}quot;Journal für Prakt. Chem.," vol. li., p. 82.

[&]quot;Annalen der Chemie und Pharmacie," vol. exxvii., p. 351, and "Comptes Rendus de l'Académie des Sciences de Vienne," June, 1864.

authors agree generally in this, that the wood contains two entirely distinct principles, one of which is nearly insoluble in water, while the other is rather readily soluble therein. The former is named morin, and the latter morintannic acid, or maclurin. Hlasiwetz and Pfaundler thus describe the operations required for the separation of these substances from each other and from the other matters contained in the wood: -The wood, previously rasped, is two or three times exhausted with boiling water, and the mixed liquors areafter having been concentrated by evaporation-left to stand for several days. A crystalline matter is slowly deposited, which has to be rapidly washed by decantation with cold water, and is next placed in a cloth and strongly pressed. This substance, which contains the principles just named, is frequently thrown down from the strong decoctions of the wood (sp. gr. 1.070), as prepared for use in dye-houses, and that deposit may serve, with great advantage, for the preparations to be mentioned. The strongly-pressed dry mass is first pulverised, and next repeatedly treated with boiling water; the remaining insoluble residue, crude morin, mixed with a small quantity of that substance combined with lime, is therefore first acted upon by dilute hydrochloric acid, well washed, and next dissolved in alcohol, from which latterafter the addition of two-thirds of its bulk of hot water—the morin separates in the form of yellow acicular crystals, which are further purified by repeated crystallisation from dilute alcohol. The morintannic acid is left in the water employed for the exhaustion of the original deposit from this solution. It is separated partly by the concentration of the solution by evaporation, and partly by the addition of hydrochloric acid; it is purified by means of repeated crystallisations from an acidulated aqueous solution. This substance is the chief constituent of the crystalline deposits seen by M. Chevreul in the blocks of the fustic.

Morintannic Acid.—The crystals of this body, as obtained by the mode of preparation just described, are yellow, but may be obtained entirely colourless by adding to the aqueous solution acetic acid and acetate of lead, and next passing a current of sulphuretted hydrogen through the liquid; the sulphide of lead, while falling down, carries along with it the small quantity of yellow colouring matter which contaminates the crystals.

This acid is very soluble in hot water, I part of the acid requiring 2'14 parts of hot and 6.4 parts of cold water for its solution; it is also soluble in alcohol, wood-spirit, and ether, fuses at 200°, and is decomposed at 250°. Sulphate of iron yields with it a greenish-black, and acetate of lead a yellow, precipitate; the latter soluble in acctic acid. It does not completely lose its water below 140°. Its composition is C₁₃H₁₀O₆. By the action of concentrated and warm solutions of caustic alkalies it is split up into phloroglucin and protocatechuic acid. A moderately concentrated solution, boiled with zinc and dilute sulphuric acid, rapidly becomes intensely red: this colouration gradually, however, fades away, leaving a wine-yellow colour (colour of Lunel or Frontignac so-called white wine). By this operation phloroglucin and a new product, machromin, are formed. The last-named substance is isolated in the following manner:-To the liquid decanted from the excess of zinc is first added the third part of its bulk of alcohol, and it is next shaken up with ether as long as that liquid becomes coloured; the ethereal solution is evaporated, the residue diluted with water, and precipitated with acetate of lead; the

ensuing precipitate is at first yellow, but gradually turns green. The filtrate contains the phloroglucin; the lead compound is suspended in boiling water, and decomposed with sulphuretted hydrogen; after filtration the liquid is evaporated in vacuo over sulphuric acid. During the evaporation the liquid, which deposits small crystals, becomes coloured; the crystals are first washed with cold water, and next dissolved in boiling dilute alcohol, from which, on cooling, they are deposited in brilliantly shining needles.

The most interesting property of machromin is its great facility of turning blue in solution, as well as in the solid state, on contact with air or under the influence of oxidising substances. The solutions of this substance yield, with hydrochloric acid, an indigo-blue precipitate; with perchloride of iron and bichloride of mercury this body developes a beautiful violet colouration, which turns gradually blue; the alkaline and ammoniacal solutions also become blue on contact with air. Machromin in solution reduces nitrate of silver to the metallic state, while the liquid assumes simultaneously a violet colour. Concentrated sulphuric acid dissolves machromin, yielding a liquid at first orange, next yellow, but which on heating turns deep green, which hue remains after dilution of the acid with water. This green liquid is turned violet by alkalies. The formula of this body is C₁₄H₁₀O₅+3H₂O; the blue material formed by the oxidation of the machromin is most readily obtained by adding to an aqueous solution of that body an excess of perchloride of iron. The blue matter precipitates in the shape of a flocculent mass, is collected on a filter, washed with water, dried and pulverised, and exhausted with ether, when it appears as an amorphous dark blue mass, soluble in alcohol, the solution having also a blue colour. This alcoholic solution, acidulated with sulphuric acid, is decolourised by the addition of zinc and sodium amalgam. The composition of this blue substance appears to be C14H8O5, or machromin less H2.

Dr. Hlasiwetz has directly prepared machromin from protocatechuic acid by reduction. When machromin in alkaline solution is treated with sodium amalgam the liquid becomes first deep brown, then red, turning finally yellow. After saturating this alkaline solution with hydrochloric acid, and shaking up with ether, the new result of the decomposition may be separated by evaporating the ethereal solution, taking up the residue with water, and precipitating it with acetate of lead. The precipitate, after having been well washed, and being decomposed with sulphuretted hydrogen, yields, on evaporation of the aqueous filtered liquid, an amorphous body, soluble in water, alcohol, and ether, and composed of $C_{14}H_{12}O_5$.

A solution of moritannic acid in sulphuric acid deposits, after having been allowed to stand for some time, a new acid called rufimoric, in the shape of a brick-red crystalline precipitate, soluble in ammonia, with a purplish colour. On being boiled with caustic potassa, rufimoric acid is re-converted into morintannic acid. Moritannic, or morintannic acid, is by some termed Maclurin. The plan of naming chemical compounds after their discoverers, or after other chemists, even if eminent, is highly objectionable, and if tolerated would become a greater nuisance than the sesquipedalian nomenclature of certain modern authorities.

Morin is nearly insoluble in cold, and very slightly soluble in boiling, water; soluble in alcohol, very slightly soluble in ether, insoluble in sulphide of

carbon. Alkalies, and soluble alkaline borates and phosphates, dissolve morin, giving yellow solutions, which are precipitated by acids. The alcoholic solution is coloured a deep olive-green by perchloride of iron. Morin

loses its water of crystallisation with great difficulty.

According to Dr. Hlasiwetz the composition of morin, dried at 200°, is $C_{12}H_8O_5$, while the air-dried substance is represented by $C_{12}H_8O_5$ 1 $_{1}_{4}H_2O$. Morin readily combines with potassa, soda, lime, baryta, oxides of zinc and lead, all these compounds being yellow. It absorbs ammonia, even so as to increase its weight by 12°7 per cent, causing the formation of a body $C_{12}H_{10}O_6+2NH_3-H_2O$. It also combines with bromine, and is readily converted into phloroglucin under the influence of nascent hydrogen or by fusion with alkalies.

It appears from the investigations made by Hlasiwetz that there exists great analogy between morin and quercetin, as may be inferred from the following brief quotations from the lengthy memoir of the author on this subject:—Both these substances yield, when treated with sodium amalgam while in an acidulated alcoholic solution, a red body; treated with the same amalgam in an alkaline solution, phloroglucin is formed; both unite with potassa and soda, as well as with zinc; both are converted by fusing caustic potassa into phloroglucin, and both withstand a high temperature and lose their water of crystallisation with difficulty.

Fustic is employed for the preparation of decoctions and more or less concentrated extracts which are used in dyeing, while it also serves for the manufacture of lakes destined for paints and for calico-printing. The shades of colours produced are nearly the same as those from quercitron, and are

equally stable.

Weld.

(French, Gaude; German, Wau; Dutch, Wouw.)

This substance is the dried herbaceous plant known botanically as Reseda luteola. It is cultivated on the Continent of Europe, but in this country has fallen into disuse; it is sown in June, and gathered the next year: the plant, which reaches about 1'3 metres in height, is brown, like grass dried in the shade, and sold in sheaves, like straw. It consists of a main stem and several smaller branches, of a yellow or greenish-yellow colour, according to the care taken in drying.

Weld is cultivated in several parts of France, in Germany, and the Austro-Hungarian empire. The colouring matter is dispersed through the entire plant, but is most accumulated towards the upper extremity and in the seeds. The decoctions of this material have a greenish-yellow colour, a sweetish-bitter taste, and a very disagreeable odour. Alkalies turn this decoction a golden-yellow; acids deepen the yellow hue; with sulphate of iron an olive-green is produced, while most of the metallic salts give yellow precipitates. Gelatin causes only an insignificant precipitate in the decoction.

Though the use of weld in this country has almost entirely ceased, mainly owing to the fact that farmers do not cultivate it here as they used to do, and on account also of the bulk of the material, we must not omit to enter into some details of the chemical history of this dye-ware, which is the oldest European yellow dye known, and was used even by the Gauls and other nations dwelling north of the Alps in the time of Julius Cæsar. The

colouring matter contained in this plant has been studied by MM. Chevreul," Moldenhauer,† and Schützenberger and Paraf.‡ The mode of extracting the colouring matter from this plant employed by the two last-named authors, is based upon the fact that luteolin is readily soluble in water, heated under pressure to 250° (equal to a pressure of about 40 atmospheres or 41.32 kilos. to the square centimetre), and crystallises, on cooling, in the shape of yellow needles, which are perfectly pure, and free from a peculiar, easily fusible, resinous matter, which accompanies the luteolin in large quantity. The raw weld is first cut up in small fragments, and exhausted in a displacement apparatus with boiling alcohol. The solution thus obtained is first concentrated by evaporation, and next precipitated by water, which throws down an abundant dirty green yellowish flocculent substance. This matter is put along with water into a glass cylinder, which is placed inside a cast-steel or a stout sheet copper cylinder, closed with a screw cap, and heated to 250° for about twenty minutes. On cooling, the slides of the glass cylinder are, for the space occupied by the water, found lined with brilliant golden needleshaped crystals, while at the bottom of the glass the resin is accumulated fused to a cake. The mother-liquor, in the midst of which this crystallisation took place, is perfectly clear and transparent. The crystals are purified by another operation of the same kind as just described, and the resin is separately submitted for two or three times to the same treatment, whereby it is entirely freed from colouring matter.

The process employed by M. Moldenhauer is the following:—The dried plant is exhausted with alcohol, and the tincture obtained is evaporated, whereby a portion of the luteolin is deposited; this substance is washed with water, and next boiled with concentrated acetic acid. Being filtered while hot this acid solution deposits the luteolin on cooling; the deposit is first washed with water, next dried in vacuo over sulphuric acid, then treated with ether, and re-dissolved in alcohol; to this solution from 24 to 28 parts of water are added, and the fluid boiled, whereby the luteolin separates in the pure crystalline state. Luteolin thus obtained is a yellow needle-shaped crystalline substance; its taste is bitter and astringent; it is free from smell, fuses at about 320°, and sublimes, undergoing a partial decomposition; it is sparingly soluble in cold, and not freely so in hot, water, but readily in alcohol and ether. Luteolin dissolves in caustic and carbonated alkaline lyes, yielding deep yellow solutions. In concentrated sulphuric acid it dissolves, yielding an orange-red liquid, from which water re-precipitates the luteolin unaltered. Luteolin is also soluble in boiling acetic and hydrochloric acids, but not in these fluids when cold; treated when dry with anhydrous phosphoric acid luteolin is converted into a red body, soluble in ammonia, with a violet colour; nitric acid converts luteolin into oxalic acid. The aqueous solutions of this dye are coloured green by perchloride of iron, and are precipitated by nearly all metallic saline solutions. The formula of luteolin, dried at 150°, is C12H8O5, and the formula of the pigment, dried over sulphuric acid in vacuo, is C₁₂H₈O₅H₂O₅; luteolin is not a glucoside. Weld or wold only yields colours upon previously mordanted fabrics. The shades

^{* &}quot;Journal de Chimie Médicale," vi., 157.

^{† &}quot;Journal für Praktische Chemie," lxx., 428. "Ann. der Chem. und Pharmacie," cxii., 107.

t "Bulletin de la Sociéte Chimique de Paris," first series, 1861, p. 18.

produced are similar to those of quercitron, but so fast as to be comparable to those of madder.

Before we enter into more details on the application of the yellow dye-stuffs treated of, we have to pay some attention to certain colouring matters resembling quercitron, and considered by some authors identical therewith, while others deny such identity; these matters are the following:—

Rutin, also called rutic or rutinic acid, melin, phytomelin. According to Hlasiwetz, this substance, obtained by MM. Weiss, Kummel, and Borntraeger from the leaves of the Ruta graveolens, does not at all differ from quercitrin, while Dr. Schunck and M. Stein* declare this opinion incorrect, and pronounce this body entirely distinct from quercitrin by its composition and properties. Melin is less coloured than quercitrin, and the percentical composition of these bodies differs considerably; melin containing in 100 parts-Carbon, 50.06; hydrogen, 5.65; but quercitrin—Carbon, 54.85; hydrogen, 5.15. Melin is also more soluble in water, hot as well as cold, as also in alcohol. The alcoholic solution of melin is precipitated by acetate of lead with a golden-yellow, but that of quercitrin with an orange-red. Melin is most readily obtained from the so-called Chinese yellow berries, the leaf buds of the Sophora japonica, which are exhausted with alcohol at 80 per cent; a small quantity of hydrated oxide of lead is first added to the solution, in order to eliminate impurities; the ensuing precipitate is filtered off, and to the filtrate is next added a larger quantity of the same oxide, and the ensuing yellow precipitate, after having been collected on a filter and washed, is suspended in alcohol and decomposed by sulphuretted hydrogen. The sulphide of lead having been filtered off, the solution yields, on evaporation, a golden-yellow crystalline substance, which is melin, and which by being boiled with dilute mineral acids is split up into glucose, and a new yellow body, melletin, somewhat like quercetin. The formula of melin is, according to M. Stein, C₁₈H₂₄O₁₂, while Zwenger and Drouke maintain that the formula of melin, a substance quite distinct from rutin, which latter they extracted from capers (Capparis spinosa) and Ruta graveolens, as well as from horsechestnuts, is C25H32O17.

Robinin has been extracted by the last-named chemists from the fresh flowers of the acacia tree, Robinia pseudoacacia. The flowers are exhausted with water, and the solution evaporated to the consistency of a syrup, then treated with alcohol; and the extract when evaporated to a small bulk deposits yellow crystals, which are washed with cold alcohol and dissolved in hot water. The solution is partially precipitated by acetate of lead, and the ensuing precipitate having been filtered off the slight excess of lead is removed by sulphuretted hydrogen from the yet hot solution, which, on cooling, deposits yellow crystals of robinin. It is a neutral, insipid substance, very sparingly soluble in cold water and alcohol, but more freely in these fluids when hot; and insoluble in ether. It fuses at 195° to an amorphous mass, which in contact with water combines therewith, and crystallises. Robinin is soluble in alkaline solutions with a yellow colour; nitric acid converts it into oxalic and picric acids. If boiled with dilute sulphuric and hydrochloric acids it is split up into an amorphous and unfermentable glucose, and into quercetin. The glucose yields, on treatment with nitric acid, oxalic and picric

^{* &}quot;Journal für Praktische Chemie," lxxxv., 351; and lxxxviii., 280.

acids. Robinin is distinguished from quercitrin by its greater solubility in boiling water, and by the colour it yields with acetate of lead; its formula is, according to Zwenger and Drouke, $C_{25}H_{30}O_{16}$.

Rhamnoxanthin.—Buchner* gives this name to a substance extracted by him from the bark of the Rhamnus cathartica, and by Phipson, from the bark and leaf buds of the Rhamnus frangula. It is a yellow crystalline substance, sparingly soluble in water, but dissolved by alcohol, ether, and alkaline solutions, with a purplish colour. It is volatile, even at common temperatures, subliming readily as a yellow crystalline body. When crude rhamnoxanthin is mixed with pure quartz sand and placed in a flask, and the mixture very gently but continuously heated, a body is sublimed which has all the appearance of alizarin, and yields with alkalies cherry-red solutions.

Colouring Matter of Thuya occidentalis.—Kawalier† has extracted from the leaves of this well-known coniferous tree a yellow body, thuyin, which, on being boiled with dilute sulphuric acid, is split up into an amorphous sugar and thuyetin:—

 $\underbrace{C_{20}H_{22}O_{12}}_{Thuyin.} + 2H_2O = \underbrace{C_6H_{12}O_6}_{Sugar.} + \underbrace{C_{14}H_{14}O_8}_{Thuyetin.}$

It is probable that the two last-named bodies are identical with quercitrin and quercetin, which they greatly resemble both in their properties and composition.

Fustet, Young Fustic, or Zante Fustic is the decorticated wood of a shrub belonging to the natural order of the Terebinthaceæ, and botanically known as Rhus cotinus, a native of southern Europe, as well as of some of the West Indian Islands. Fustet is a hard, compact, beautifully yellow wood, imported in bundles and small fagots. The American fustet is more valued than the Italian growth. The wood contains—(1) a crystalline yellow colouring matter; (2) a red substance; (3) a brown astringent principle. The vellow colouring matter was first isolated by M. Chevreul, who named it fustin. Dr. Bolley has more recently investigated this substance, which he considers as identical with quercetin, and prepares as follows: !-- The aqueous decoction of the wood is evaporated to dryness; the residue treated with alcohol, the insoluble matter retains the red pigment; the alcoholic solution is concentrated by evaporation and mixed with water, whereby the yellow principle is precipitated as a crystalline crust, which after washing with cold water is re-dissolved in alcohol and re-precipitated with water, thus yielding the pure material. Although fustin thus prepared in many respects resembles quercetin it differs from the latter in some respects, yielding, for instance, an orange, and not, like quercetin, a yellow precipitate with protochloride of tin; the alkaline solutions of fustin are red. Dr. Bolley feels inclined to ascribe these differences to a small quantity of the red colouring compounds. Still the identity of quercetin and fustin is not at all proved, and requires further investigation. The fustet red has never been examined, and is probably due to an alteration of the yellow principle. The decoction of fustet exhibits the following reactions:-Its colour is orange-yellow; alkalies turn it red;

^{* &}quot;Journal de Pharmacie" [3], xxiv., 50; and Dingler's "Polytechn. Journal," 1865, clxxxviii., p. 143.

[†] Kawalier, "Comptes Rendus de l'Académie de Vienne, xxix., 10.

t "Bulletin de la Société Chimique de Paris," ii., 479. Schweitzerische, "Polytechnische Zeitschrift," ix., 22.

alkaline earths redden it, and cause a precipitate; tin crystals and acetate of lead yield orange precipitates; acetate of copper a chestnut red-brown precipitate; acids turn the colour a greenish yellow. Fustet is chiefly used for dyeing wool and some kinds of skins, and is also, though rarely, used as a tanning material. With aluminous mordants it yields an orange-yellow colour, and with tin mordants an orange-red. These colours are, however, fugitive, and are altered by the action of alkalies and soap; fustet is not applied in calico printing, and very little in cotton dyeing.

Colouring Matter from Buckwheat (Polygonum Fagopyrum).*

Dr. Schunck has extracted from the leaves of this plant a vellow crystalline colouring matter, sparingly soluble in cold, more readily so in hot, water; readily soluble in alcohol, concentrated sulphuric and hydrochloric acids, and in alkalies. According to the author, the formula of this substance is C₁₅H₂₀O₁₀, and he considers it identical with rutin, and also with the ilixanthin (obtained from the leaves of the holly, Ilex aquifolium). The aqueous solutions of this substance yield, on the addition of acetate of alumina and acetate of lead, vellow precipitates; with acetate of copper a greenish yellow; and with perchloride of iron an olive-brown precipitate; this dye yields, on previously mordanted cotton, bright yellow shades. The pure dye is obtained by making a decoction of the leaves, to which while boiling a small proportion of a solution of acetate of lead is added, in order to precipitate thereby some other vegetable principles; the liquid is filtered while still boiling; hot acetic acid is next added, whereupon the pure material is deposited in the shape of small acicular crystals.† The bark and root of the pomegranate contain beside tannin a yellow colouring matter, which has not been hitherto scientifically investigated, but which, judging from its behaviour in dyeing, approaches to quercitrin and quercetin. It is used by dyers to a small extent for certain shades of drab and grey. The husk or rind of the pomegranate fruit is rarely used in this country as a source of tannin, though it contains upwards of 30 per cent of tannic acid, and it yields with iron mordants rich, bloomy blacks, and is used in Spain in preference to sumach both for dyeing and tanning. As regards the use made in dyeing and printing of the yellow colouring matters belonging to the quercetric group, it is evident that the great analogy in properties, composition, and chemical behaviour of these principles must extend to their application as dye materials, but although this is actually so, it is not in practice indifferent whether the one or the other be used, and this is chiefly due to the fact that the practical dyer does not employ the pure tinctorial principles, but either the vegetable matter in its native state or aqueous extracts, which are complex substances containing impurities, which in various ways affect the applicability of the dyeing process.

The following is the general outline of the use of these colours:—None of them can be fixed without the aid of a mordant whatever may be the nature of the fibre. With aluminous or tin mordants the tissues are dyed yellow, orange-yellow, or nankin-yellow, according to the strength of the mordant. With iron the shades obtained vary from grey to olive-green or black. With mixed iron and alumina mordants olive and reseda-yellow colours are

^{* &}quot;Dingler's "Polytechn. Journal," cxv., 157.

^{1 &}quot;Répertoire de Chimie Pure," i., p. 438. "Chemical Gazette," Nos. 399 and 201.

produced. With chromium mordants an olive-yellow is produced. These shades are the same upon cotton, silk, and wool, but vary slightly within narrow limits. In dyeing there are employed—(1) the raw vegetable material as it occurs in commerce, generally in the state of a more or less finely pulverised substance; (2) the same material after having been previously treated with dilute and boiling sulphuric acid, the product of this action yields richer and brighter colours, but requires in dyeing a higher temperature, and as a consequence thereof the portions of the fabric intended to be left white are more soiled. When the dye material contains tannin in larger quantity, as is the case with quercitron, fustic, and others, it is best to add to the materials of the dye-beck a sufficient quantity of gelatin, in order to neutralise the effects of the tannin.

Calico is now very generally dyed yellow with quercitron or quercetin, but formerly weld was used, and with the advantage that it yielded faster colours. As regards cotton or calico, previously printed and mordanted, and treated as described for madder, the pieces, four at a time, are placed in a dye-beck, containing per piece, from 750 to 1500 grms. of quercitron, and 60 grms. of glue to each 500 grms. of the last-named substance. The colouring matter dissolves so readily that the goods can be put in the beck immediately after the addition of the dye-ware. The process is commenced at the ordinary temperature of the air; the heat of the contents of the dye-beck is raised in an hour's time to from 38° to about 57°, but for greys the temperature should not exceed 38°. On being taken from the dye-beck the pieces are first thoroughly washed and rinsed in cold water, and next put for a quarter of an hour in a bath of bran, containing 21 kilos. of bran per piece, and at a temperature of from 38° to 51°. If the patterns have much white this operation has to be repeated twice, the object being to clear and brighten the grounds. This branning is the only clearing which this dye-ware will bear.

Dyeing with Weld.—The plant is first boiled in the dye-beck for about half an hour; it is then removed, and the contents of the beck allowed to cool down to about 63°; at this heat the goods are entered, four or six pieces at a time. The quantity of weld applied varies from 5 to 10 kilos. per piece, according as the pattern printed on the fabric is more or less heavy; when a white ground is required, and the pattern is light, it is as well to add about 60 grms. of glue for each half kilo. of weld. The temperature of the dyebeck is raised in half an hour's time to 75°; on being removed from the beck the goods are twice branned, the quantity of bran to be 5 kilos. per piece for white ground, and 2½ kilos. per piece for yellow ground. After this the pieces are grass bleached for a few days, and next passed through dry bran. The use of weld (although discontinued in this country) has the advantage of leaving the whites purer and more readily cleared than is the case with quercitron. Pomegranate bark is employed like weld, that is to say, boiled in the beck previous to use.

Fast cinnamon-yellow or brown shades in the madder style are often first dyed with quercitron and bablah,* or quercitron and pomegranate bark. Where

^{*} This is the name (also babula or Neb-nab) of a fruit imported from Senegal and India; it was, when first imported, said to have the property of imparting permanency to all dyed colours, but this was found to be an exaggeration. Bablah contains tannic and gallic acids in large quantity, and may be used as a substitute for sumach.

a myrtle-green coloured ground is required, the goods are first dyed with quercitron and pomegranate bark, and next with Brazil wood. It is evident that by varying the nature of the mordant and that of the dye-ware to be superimposed on the yellow, olive, or grey produced by quercitron or its allies, it is easy to produce a series of various shades and colourations too many to be here enumerated. Among the more important of these mixtures are those by which greens are produced with yellow and blue, about which more will be said when we shall have treated of blue colours.

We confine our observations here to the following:—When a fabric, previously dyed a vat blue, is mordanted with acetate of alumina, and next dyed with quercitron, weld, or berries, it assumes a green shade; and when a mixture is made of such materials as will produce steam blue and steam yellow, the result will be the production of a green: this, except the Chinese green, "Lo-kao," and the aniline green, is the only means of producing upon

fabrics a green dye of organic origin.

When cotton yarn has to be dyed yellow it is first sumached, next mordanted with red liquor (sp. gr. 1.014), squeezed, and immediately placed in a hot quercitron bath, to which tin-salt has been added; the cotton is next washed and dried. For greens the yarn is mordanted with solution of acetate of alumina (sp. gr. 1.034), squeezed, washed with warm water, dyed with quercitron, aged, mordanted with weak red liquor, well squeezed, and next dyed with extract of indigo. Silk is dyed yellow with quercitron by the following process:-It is first mordanted with alum (1 part of alum and 10 of water), next dyed in a quercitron bath, to which alum or tin-salt has been added, and the fabric next cleared with soap. If weld or fustic is applied the same process is used for silk; and if it is desired to produce green it is first dyed yellow, and next indigo carmine is added to the contents of the dye-beck. Wool is first mordanted in a boiling-hot bath, made up of cream of tartar and alum, or of 2 kilos. of alum and 20 grms. of sulphuric acid for 10 kilos. of wool; the specific mordant for wool or yellow spirit consists of 4 kilos. of water, 4 kilos. of sulphuric acid, and I kilo. of tin crystals.

In steam- and application-colours the more or less concentrated decoctions of the yellow dye-ware are frequently used upon cotton, wool, mixed fabrics, and silk; these decoctions yield when alone, and with suitable mordants, the same shades as when applied in the dye-beck; and in association with other dye materials for either red or blue or other colours, a large and varying series of tints are produced. Decoction of Persian berries is often preferred for this purpose, on account of the greater solubility of its colouring matter, and also because that pigment has not, as is the case with quercitron, a tendency, when in decoction, to separate from the liquid. Extracts of fustic are little used except in mixtures, as for green, because the yellow pigment of this ware is not pure enough for use by itself in the steaming process, and has a tendency to become rust-coloured.

Upon Cotton.—The fixing basis for yellow matter is alumina, to which are added sometimes tin preparations, and sometimes also preparations of

copper, these latter playing a secondary part and acting as oxidisers.

The following are the chief substances in use for steam-yellows:—Extracts of quercitron, Persian berries, and fustic. The mordants are—Acetate of alumina (weak red liquor, as for madder); small quantities of proto- and

ALOES.

bi-chloride of tin, but always in small quantity as compared with the alumina, since it is employed more as an alterant than as a mordant; thickeners; various other materials, e.g., acetic acid, are added, though not absolutely necessary. The goods are previously prepared with alumina or stannate

of soda.

Application-Yellows are generally prepared with berries and tin-salts, while alumina is the mordant.

Steam Reseda-Yellow: made up with quercitron extract, pyrolignite of iron, and an aluminous mordant.

Steam-Grey is chiefly made up of quercitron extract, extract of Brazil wood, decoction of nutgalls, sulphate of iron, pyroligneous acid, and bichromate of potassa; or extracts of Brazil wood and quercitron, with pyrolignite of iron, acetate of iron, and berry liquor; or acetate of iron, alum, berry liquor, decoction of nut-galls.

Steam-Olive is made up of berry liquor, acetate of iron, and tin-salt.

Steam-Brown (Puce) is mainly made up of mixed extracts of Lima and St. Martha woods, quercitron, pyrolignite of alumina, chlorate of potassa; also of berry liquor, fustic, and Lima wood decoctions, red liquor, acetate of copper, sal-ammoniac—this latter material acting, during the printing process, in a physical manner, and during the oxidation chemically, somewhat as in aniline-black.

Application-Puce is made up of berry liquor, Lima wood extract, bichloride and protochloride of tin, and nitrate of iron.

Steam-Orange is made up of berry liquor and extract of St. Martha wood, an aluminous mordant, and acetate of copper.

Application-Orange is chiefly made up of berries, St. Martha wood, and bichloride of tin.

Steam-Greens are prepared by a mixture of steam-blue with berry liquor, red liquor (as used for madder), and tin-salts.

The steam-yellows are fixed upon wool and silk by means of a mixture of alum, the chlorides of tin, and oxalic acid.

Aloes.

Aloes, or aloe resin, is the inspissated dry juice of a plant belonging to the Asphodeleæ, a native of the Cape of Good Hope, and cultivated in India and the West Indies, as well as some parts of Southern Europe. The juice is best obtained by cutting off the leaves at their bases, and causing the sap to run into any suitable vessel over which the leaves are hung up. The juice becomes dry by exposure to air, and is found in commerce as a resinous mass, of a yellowish-brown colour, and very bitter taste.

There are several varieties of aloes, the chief being-

Cape aloes, the product of the Aloe spicata, arborescens, and lingua.

Socotrin aloes, the product of the Aloe socotrina, a highly-valued variety.

Aloe hepatica, the product of several species of aloe plants, and chiefly imported from Greece and Egypt.

Barbados and Curaçoa aloes, obtained from the Aloe arborescens by steeping the leaves first in boiling water, and next pressing them.

Aloes is imported in boxes or bags, and very largely used, especially in veterinary medicine. The colour of the pulverised resin is yellow to brownish-

yellow, and it emits an aromatic yet nauseous odour. The aloes contains—A yellow crystalline principle, soluble in cold water, and named aloin; a resinous-looking substance, soluble in boiling water, and called aloctin. The first-named substance, also known as aloes bitter, is best obtained by exhausting Barbados aloes with cold water, after having previously mixed it with sand, so as to prevent it from caking together. The solution yields, on evaporation to a syrupy consistence, and after standing for a few weeks, a crystalline deposit. The other varieties of aloes do not yield, when treated as described, an aqueous extract of sufficient purity to obtain therefrom aloin in a crystalline state. The latter substance has the following properties:—It forms prismatic crystals, tasting at first sweetish, but with a very bitter after flavour; sparingly soluble in cold water and cold alcohol, more readily in these fluids when hot; neutral to test-paper; solutions bright yellow, becoming orange upon the addition of alkalies; formula, according to Dr. Stenhouse, $C_{17}H_{18}O_7$.

Aloetin, or aloes resin, is viewed by Winkler as an acid, and by M. Bley as a mixture of two acids: it is insoluble in cold, but readily soluble in hot, water.

According to M. Ulex, commercial aloes consists, in 100 parts, of—Aloin, 69.2; aloetin, 25.6; albumen, 5.2. Dr. Kossmann* found that Cape aloes contains chiefly two substances, one of which is soluble in water, and the other insoluble therein, while both, on being treated with very dilute boiling sulphuric acid, are split up into glucose and several resinous substances, which act as acids. He finds that the aloetic principle is very readily oxidisable, especially so in the presence of alkalies. The composition of the soluble portion of the aloes is $C_{17}H_{22}O_{10}$, and by being split up by sulphuric acid it yields aloeretic acid, being a resinous matter, formula $C_{15}H_{16}O_7$, and aloeretin, $C_{15}H_{24}O_{20}$, which the above-named author considers as a product of the oxidation of aloeretic acid.

The aloin of Stenhouse is the substance which is primitively present in the lactiferous vessels and cells of the Aloe spicata, and is originally a crystalline and almost colourless substance, but by the action of air, water, and heat, becomes brown and amorphous.† This substance, insoluble in water, has, according to Dr. Kossmann, the composition $C_{51}H_{60}O_{27}$, and on being treated with boiling dilute sulphuric acid it yields glucose and aloeresinic acid, $C_{15}H_{16}O_6$. The aloin as originally present in the juice of the plant, $3C_{17}H_{18}O_7$, yields, by hydratation and oxidation, products insoluble in water, and others soluble:—

$$3C_{17}H_{18}O_7 + O_3 + 6H_2O = \underbrace{3C_{17}H_{22}O_{10}}_{\text{Soluble aloin,}}; \ 3C_{17}H_{18}O_7 + O_3 + 3H_2O = \underbrace{C_{51}H_{60}O_{27}}_{\text{Insoluble aloin.}}$$

When treated with nitric acid, aloin yields several nitrated coloured compounds, and in the first place aloetic acid—prepared by heating, upon a waterbath, I part of aloes of commerce with 8 parts of nitric acid (sp. gr. 1'31): the vessel containing the mixture is withdrawn from the water-bath as soon as

^{* &}quot;Journal de Pharmacie et de Chimie," September, 1861. "Répertoire de Chimie Pure," vol. v., 1863, p. 530.

[†] Our readers may be reminded that the ornamental plant commonly called aloe by nurserymen is not an aloe, but an Agave, and entirely different from the aloe here spoken of.

effervescence sets in, and when this ceases cold water is added, whereby a yellow powder is thrown down, consisting of a mixture of aloetic and chrysammic acids, which may be separated by utilising the property of the latter of being insoluble in boiling alcohol, or also by first converting the joint acids into potassa salts, and making use of the insolubility of the chrysammate of potassa in water.

Aloetic acid is an orange-yellow, crystalline, pulverulent, bitter substance, sparingly soluble in cold water, more readily so in boiling water and boiling alcohol. Its solutions in caustic alkalies are red, while it yields with ammonia a violet solution which contains an amide. The alkaline aloetates are crystalline and soluble in water, but the other aloetates are insoluble. The formula of aloetic acid is $C_7H_2(NO_2)_2O$.

When aloes is treated with an excess of boiling and concentrated nitric acid, it is converted into chrysammic acid, $C_7H_2(NO_2)_2O_2$. According to Dr. Sace* this acid is prepared for industrial purposes as follows:—8 kilos. of nitric acid (sp. gr. 1·31) are heated on a water-bath, with the addition of 1 kilo. of aloes in lumps: when the effervescence at first ensuing is finished, another kilo. of nitric acid is added, and the heating is continued as long as any gas is given off; the liquid is then poured into cold water; the acid, which separates as a flocculent matter, is washed first by decantation, and next on a filter, until the filtrate begins to assume a purplish colour: the quantity of chrysammic acid obtained amounts to about 45 grms.: there are also oxalic and picric acids formed during this reaction.

Chrysammic acid is a crystalline, beautifully golden-yellow substance, almost insoluble in cold water, to which it imparts, however, a fine purple colour; it is readily soluble in alcohol and ether; the chrysammates are sparingly soluble in water, and when crystalline display a golden-greenish hue. Chrysammic acid explodes if suddenly heated; sulphuric acid decomposes it, causing an abundant evolution of gas and the production of a violet substance, which, by the addition of ammonia, yields an insoluble blue and a similarly coloured soluble matter. The alkaline sulphides convert chrysammic acid, in potassic solution, into a blue crystalline compound (hydrochrysamide), insoluble in water and alcohol. Ammonia forms, with chrysammic acid, two amides, viz., chrysamide, a crystalline brownish-red substance, with a metallic hue, and chrysamidic acid, a deep olive-green matter.

The first attempts to apply industrially the colouring matters contained in aloes, and those which are its products of decomposition, were made in France, by Boutin in 1840, E. Robiquet in 1847, and Sacc in 1854. The results obtained may be summarised as follows:—An aqueous decoction of aloe yields, upon cotton, with acetate of alumina as mordant, and followed by steaming, a pale nutty colour; upon wool, a canary-yellow; with pyrolignite of iron this decoction gives upon cotton a deep nut-colour, upon wool a bright bistre-brown; with aluminate of soda the decoction produces upon cotton a very bright nut-colour, and with stannate of soda a bright dust-grey colour. When aloes decoction and nitric acid or ammonia are mixed, wool is dyed a deep brown; aloetic acid yields upon wool a full deep brown colour, which becomes brighter by being passed through a very weak solution of bichloride of tin, and turns deep bistre-brown when passed through a solution

^{* &}quot;Bulletins de la Soc. de Mulhouse," vol. xxvi., p. 149 and following

of protochloride of tin. A solution of aloetate of ammonia yields upon wool a deep moss-green colour, and upon cotton a mouse-grey colour, which resists washing with soap: when bichloride of tin is added to this bath, wool is coloured deep bistre-brown; and with addition of acetate of alumina the same bath produces upon wool a good moss-green, and upon cotton a good grey colour. When woollen fabrics are steeped in a solution of aloetate of ammonia, and dried in the air, a solid green is produced.

Chrysammic acid by itself dyes wool a deep rich brown and silk a purplish-brown; chrysammate of soda dyes wool cinnamon-brown; with aluminous mordants chrysammic acid yields a beautiful violet, which, however, does not resist soap well. Previously stannated cotton tissues are dyed grey by chrysammic acid, while upon the same fabric without any mordant at all it yields a nut-colour; chrysammate of ammonia yields, with the addition of bichloride of tin, a salmon upon cotton.

It does not appear that at present either aloes or chrysammic acid are used, and in this country their application has never been extensive.

Turmeric.

The substance known in commerce as turmeric root is the underground stem (tuber) of a plant belonging to the Scitamineæ, and botanically known as Curcuma tinctoria or longa. The shape of this article of commerce, which grows in a wild state in some parts of China and India, is sometimes cylindrical, but more frequently ovoid; its epidermis is yellowish-grey, while within the colour is a bright yellow; it emits a strong odour, and its taste is peppery, aromatic, and bitter at the same time.

The plant producing this root is cultivated in Java and Bengal, the latter

country producing the better quality.

According to the Japanese there exists a variety of turmeric, known by them as Yo-kin, yielding a root of about the thickness of a finger, and only about an inch in length, and distinguished externally by transverse stripes of a brownish hue.

Turmeric contains, according to Vogel and Pelletier, ligneous matter, starch, and a yellow colouring substance; while Dr. Schützenberger found therein a quantity of pectic acid and pectin. The colouring matter of turmeric is very sparingly soluble in water, but alcohol, ether, the fatty and essential oils, dissolve it readily. The alcoholic solution of turmeric is thrown down, by the addition of tin crystals, as a red precipitate; by acetate of lead, a chestnut-brown; by mercury salts, reddish-yellow; salts of iron colour the tincure brown; alkalies turn it brown; weak acids do not act upon the pigment, which is turned red by concentrated acids. The colouring matter of turmeric has received the name of curcumin.

We shall first give a brief review of the researches made upon this substance by Vogel, Pelletier, Schlumberger, and others, and then communicate the results of certain researches just published, which in a great measure contradict the results obtained by the chemists just named.

Curcumin may be prepared by first exhausting the pulverised turmeric with water; the substance is next dried, and afterwards exhausted with sulphide of carbon, which only dissolves fatty and resinous matters, but leaves the pigment untouched. The residual matter is further treated either with boiling alcohol

or alkaline lye: in the first case the alcoholic fluid is evaporated to dryness, and the remaining extract taken up with ether, which dissolves the colouring matter; or, in case an alkali has been used, the pigment is precipitated by hydrochloric acid, the sediment washed and dried, and next treated with ether. The pigment obtained by the evaporation of the ethereal solution can be further purified by re-solution in alcohol, precipitation by acetate of lead, and decomposition of the precipitate so obtained by sulphuretted hydrogen. The mixture of sulphide of lead and curcumin is dried and taken up with ether, which, on evaporation, yields curcumin, as a translucent, amorphous, cinnamon-coloured mass, which when powdered appears yellow. It is soluble in ether, alcohol, alkalies, and concentrated acids, the alkaline solutions being of a red-brown colour.*

M. E. Schlumberger has been the first to investigate the modifying action of boracic acid upon curcumin. It is well known that turmeric paper becomes brown under the joint influence of the boracic and any mineral acid, preferably the hydrochloric. Ammonia turns this colour blue. When an alcoholic solution of curcumin is boiled with boracic acid its colour turns orange, and upon the addition of water to the previously cooled solution a vermillioncoloured powder is thrown down, being a compound of the pigment with boracic acid. This combination is broken up by the sufficiently prolonged action of water; the boracic acid dissolves, and there remains a yellow resinous matter which differs from curcumin, inasmuch as it does not yield a red colouration with boracic and hydrochloric acids, and on being dissolved in alkalies gives a greenish-grey colouration. The boracic compound of curcumin dissolves with a purplish-violet colour in alkalies, but this soon turns to grey. When hydrochloric acid is added to an alcoholic solution of bromocurcumin, and the fluid boiled, it rapidly assumes a blood-red tint; on cooling a new body is thrown down, while the boracic acid remains in solution. The substance so deposited is first washed with dilute alcohol, next with pure water, in order to eliminate all boracic acid; the residue is dried, and next dissolved in a boiling mixture of 2 parts of alcohol and 1 part of acetic acid. This fluid, being filtered while hot, deposits on cooling rosocyanin, while the pseudocurcumin remains in solution. By pseudocurcumin is understood the organic resinoid substance resulting from the prolonged action of water upon borocurcumin, just above mentioned. The rosocyanin is first dried, and next treated with ether, in order to remove the last traces of yellow colouring matter: thus purified, it is a crystalline substance, of a cantharides-like lustre, insoluble in water, ether, and benzol, but very soluble in alcohol, to which it imparts a most magnificent deep rose-red, quite comparable to fuchsin solutions. This fluid becomes permanently yellow on being boiled. Ammonia turns the alcoholic solution of rosocyanin a splendid blue, but this colouration changes shortly into a dirty grey; acids turn the blue ammoniacal solution red again; lime- and baryta-water yield blue precipitates in the alcoholic solutions, which do not contain any boracic acid at all.

The relations existing between curcumin and rosocyanin (also called roseocyanin) and pseudocurcumin are unknown, neither was until July, 1870, the

^{* &}quot;Journal de Pharmacie," vol. ii. (2). p.20. Lepage, "Journal des Connaissances Médicales et Pharmaceutiques," vol. xxvi., p. 315. "Réportoire de Chimie Appliques," vol. i., p. 304.

true composition of curcumin known.* It is very probable that the phenomena of colouration as exhibited by curcumin, which turns red and blue, and then yellow again, under the action of comparatively weak reagents, bear a relation to certain phenomena observed with flowers.

It is not impossible that the roseocyanin of M. Schlumberger is identical with the red colouring matter of flowers or cyanin investigated by MM. Frémy and Cloëz, which latter substance is turned also blue by alkalies. If this suggestion proves correct, on more precise investigation, turmeric could become a useful source of preparation of the red colouring matter of flowers, which it is very difficult to obtain by direct extraction.

Although turmeric is rich in colouring matter, its want of permanence is a hindrance to its application as a dye-material. Some time back the use of turmeric was almost exclusively limited to printing and dyeing silks. It is now employed to a vast extent in stuff-dyeing, forming an important constituent in certain compound colours, especially the so-called "sour browns."

Turmeric is generally sold in powder, and is sometimes sophisticated with common salt, which gives it a brighter appearance in the mass, but interferes with its uses. It should be quite dry; if damp it loses its colour, turns a yellowish-brown, and dyes flat shades. The safest method of testing samples is to dye equal weights of white woollen cloth with equal weights of the turmerics. The swatches are then compared, not only for depth of colour, but are held up horizontally to the light and viewed along the surface. In this "over-hand" position a good turmeric should show a beautiful golden lustre, on the purity of which its value depends for many purposes, i.e., for yellows on the cotton warps of figured table-covers. In India it is used for colouring rice. It serves to make the well-known yellow test-paper for chemical use. The Chinese use kiang-hoang (the vernacular for turmeric) for dyeing silk vellow; it is the cheapest yellow dye, but of course very fugitive. The dyeing process is done as follows:—The pulverised turmeric is treated with boiling water, and the mixture well stirred up; the fluid, having become clear, is decanted from the dregs, and in the fluid the silk is immersed after addition of lime-juice.

The colouring matter of turmeric fixes directly upon wool, silk, and cotton, it being only required to put the tissue in a boiling decocion of the ware. By printing on tissues an alcoholic or acetic solution of curcumin, and steaming, the colour is also fixed.

M. Persoz has obtained good results by mixing an emulsion of carbonate of soda and Gallipoli oil with a solution of curcumin in Gallipoli oil, and using this mixture for printing. After drying, the fabrics are passed through an acid. When a pattern is printed on silk by means of an aluminous and an iron mordant, und the silk so prepared first put in a dye-beck containing Brazil wood, and next in a turmeric bath, the patterns will come out red and black upon a yellow ground.

We now turn our attention to the recently-made researches on curcumin by M. F. W. Daube.† This author has succeeded in preparing pure and crystal-line curcumin by the following process:—The root, coarsely pulverised, is first submitted to a process of steaming, to get rid of the essential oil; it is next

^{* &}quot;Bulletins de la Société Chimique de Paris," 2nd series, vol. v., p. 194.

^{+ &}quot;Berichte der Deutschen Chemischen Gesellschaft zu Berlin," third year, p. 609 and following.

washed with boiling water as long as that fluid becomes coloured; the material is then strongly pressed, and dried. The dry residue is treated with boiling benzol, which, on cooling, deposits crude curcumin. The author finds it absolutely necessary to use benzol, although it is a bad solvent for curcumin, I part requiring 2000 parts of boiling benzol for solution; but only by its use is it possible to prevent the solution of a resinous matter present in the root. The crude curcumin so obtained is dried by pressure between folds of blottingpaper, and next dissolved in alcohol, whereby a small quantity of a yellow flocculent matter remains undissolved: the alcoholic solution is filtered, and next precipitated by means of an alcoholic solution of acetate of lead; the red precipitate of plumbo-curcumin is first washed with alcohol, next decomposed by means of sulphuretted hydrogen, after having been suspended in water: the pigment, curcumin, remaining mixed with the sulphide of lead, is extracted by means of boiling alcohol, and this solution, having been left to evaporate spontaneously, leaves curcumin as a prismatic crystalline body, incapable of sublimation. It fuses at 165°, and is decomposed when heated to a higher temperature. Curcumin is most soluble in alcohol and ether; concentrated mineral acids dissolve some curcumin, but do not leave it unchanged. Alkalies dissolve it, the solutions exhibiting a bright red-brown colour; acids reprecipitate the curcumin. With compounds of lime and baryta, curcumin yields reddish-brown precipitates. The formula of curcumin is C10H10O3, and that of the lead compound C20H18PbO. When treated with nitric acid, curcumin yields oxalic acid. The curcumin obtained by the author exhibits, in a high degree the reactions above mentioned with alkalies and boracic acid. The author has obtained rosocyanin from his pure curcumin, but his researches in this direction are not yet complete: the substance hitherto known as curcumin, and above described, is, according to the author, a mixture of resinous matters and curcumin.

Yellow Colouring Matters of Chinese Origin.

Dr. Rondot, in his work on the Chinese-green, enumerates the following yellow dye-wares of vegetable origin as more particularly used in China:—

The Hohang-teng (yellow-weed) is a kind of reed or rush, of from 0.010 to 0.015 metre diameter; its taste is bitter; its shape cylindrical and knotty; externally the colour is reddish-brown, internally bright yellow. This substance seems to be the produce of the Menispermum tinctorium or of the Cocculus fibraurea tinctoria (tien-sien-tan of the Chinese and the cayvang-dang of the Cochin Chinese). This substance yields its colouring matter to boiling water, and dyes tissues without any mordant. It is used to give a ground to fabrics intended to be dyed yellow with safflower.

The Hoang-pé-pi, the bark of the hoang-pé-mou, in all probability the bark of the Pterocarpus flavus or of a species of Hymenolobium, is a tree growing to great height in some parts of China. This ware likewise yields its pigment to water, and dyes cloth a reddish-yellow.

The Ti-hoang is the root of a plant, probably the Rhamnesia sinensis. Its colour is similar to that of our common carrot internally.

Wongsky, Wongshy, Wongschy, Hoang-tchy, is the fruit of the Gardenia grandiflora, a substance which has been investigated by Stein,* Von Orth, 1

^{* &}quot;Chem. Pharm. Centralblatt," No. 9, p. 140.

^{+ &}quot; Neues Repertorium für Pharm., iv., 12-17.

F. Rochleder,* and also Th. Martius Mayer. According to Dr. Rochleder it contains pectin, rubichloric acid, tannin, and a yellow colouring matter identical with the crocin present in saffron (Crocus sativus). This pigment is obtained by exhausting the wongshy with boiling alcohol, and concentrating the liquid by evaporation, followed by filtration. The alcoholic tincture is then diluted with much water, and there is added gelatinous alumina. After a few days standing the liquid is again filtered, and the filtrate precipitated with acetate of lead. The precipitate thus formed is washed with cold water, and, after having been suspended in water, is decomposed by sulphuretted hydrogen. The colouring matter is extracted from the sulphide of lead by means of alcohol, the liquid evaporated to dryness and taken up with water, by which the colouring matter is left undissolved as an amorphous rose-coloured body, about which more will be said under "saffron."

Wongshy is used in China for dyeing yellow, and also as a ground for green dyes, and for imparting a first colour to silk and cotton which are intended to be dyed cherry-red, scarlet, or crimson, with safflower. The colours thus obtained are faster and brighter. Wongshy is not much used as a dye-material in this country: it produces shades of yellow and orange upon woollen and silk which do not appear to be possessed of much stability.

The late M. Persoz made some experiments with the colouring matter of the hoang-tchy, which he obtained from the late celebrated botanist Dr. Martius. Persoz exhausted the fruit first with sulphide of carbon, which takes up a fatty matter; next with wood-spirit (methylic alcohol), which dissolves the colouring matter, leaving it on evaporation as a reddish crystalline residue, soluble in water. This colouring matter dyes cotton, mordanted with alumina or oxide of tin, a yellow colour; with oxide of iron an olive colour is obtained. This colouring matter dyes silk directly without any mordant. The decoction of the fruit was used, and to each litre thereof were added 2 grms. of alum and 1 grm. of oxalic acid; temperature, 40° to 50°: the shade obtained is pure yellow, not affected by acids or alkalies: wool is dyed similarly, with the addition to the bath of a tin-salt, or the wool may be first alumed.

The name of hoang-tchi applies to the yellow colouring principle of saf-flower, which is extracted by first placing the safflower (previously tied in bags) in pure water, and squeezing it by stamping on it with the naked feet; and next by placing it in sour rice-water. The yellow juice thus obtained is employed for imparting a ground to silk intended to be dyed scarlet and red. Since Chinese safflower is not brought into commerce until after it has been treated as just described, it is clear that the ware imported from China is almost entirely deprived of its yellow colouring principle. According to the Chinese the fastness and beauty of their safflower-dyed fabrics is due to the fact that they first dye these fabrics a yellow colour, as just mentioned.

Saffron.

What is known as saffron is the pistils and stigmata of the flower of the Crocus sativus, a bulbous plant of the liliaceous order, which is a native of Southern Europe, and cultivated—for its use in pharmacy and as a condiment—in Spain, Southern France, Austria, Greece, and England. This ware contains

^{* &}quot;Neues Repertorium für Pharm.," iv., 365-367. "Dingler's Polytechnisches Journal," cxiv., 136. "Répertoire de Chimie Appliq.," i., 87.

a pigment identical with that already described as present in the wongshy, or fruit of the *Gardenia grandiflora*. The colour of saffron may be obtained from it by first exhausting with ether, whereby fatty and resinous matters are removed, and treating the residue with water; the aqueous solution is precitated with acetate of lead, and the precipitate is treated as directed for that similarly obtained from wongshy.

Crocin is a rose-coloured inodorous powder, which turns brown by heat, and is decomposed at 200°; it is soluble in water, alcohol, and alkaline solutions, imparting to them an orange colour. Crocin is hardly soluble in ether; strong sulphuric acid dissolves it, the liquid assuming first a blue, next a violet colour. Boiling with dilute sulphuric acid splits crocin up into glucose and crocetin, an amorphous deep red substance, almost insoluble in water, but soluble in alcohol. Its formula is stated to be $C_{20}H_{26}O_{11}$.

Barberry Bark.

The substance known as barberry bark and root is obtained from the Berberis vulgaris, a native shrub of Central Europe, and growing wild even in India: it is used as a dye-material, and contains a yellow pigment, chiefly accumulated in the bark, but met with in the wood as well as the root of the shrub, which latter bears some likeness in outward appearance to ipecacuanha. The colour of the root is yellowish, and its taste bitter. The colouring principle of the barberry differs very essentially from the other yellow dies, inasmuch as berberine is a nitrogenous substance,—in fact, an alkaloid,—and is also met with in Colombo root, in the root of Cocculus palmatus, and also, according to M. Dyson Perrins, in the Hydastis canadensis, to the extent of 4 per cent; the yellow Assam wood (Woodumpar), of which the only specimen present in Europe is at the India Museum; a peculiar root from Rio Grande, Brazil; the yellow bark from Bogota (7 per cent), from the Pachnelo, a vegetable product, of which only one sample exists at the Kew Botanical Museum; the Coptis tecta, or Mahmira, a ranunculaceous plant, native of Hindostan and China (8 per cent).

The substance which MM. Chevallier and Pelleton extracted from the Xanthoxylum clava Herculis, a shrub belonging to the Rutaceæ, is nothing else than berberine. Berberine may be obtained from the root by adding, to a previously concentrated aqueous decoction, alcohol, which precipitates foreign matters. The liquid is filtered, and the alcohol removed by distillation; after some time the concentrated fluid deposits yellow needles of berberin, which are purified by re-crystallisation from water.

The commercial extracts of barberry root and bark deposit, on standing, crystals of berberine, which the root contains to an amount of 1.3 per cent.

Berberine has the following properties:—It forms yellow, silky, needle-shaped crystals, soluble in 500 parts of water at 12°, very soluble in hot water and hot alcohol, insoluble in ether; its salts are yellow, and generally not very soluble; nascent hydrogen converts it into a colourless basic substance, $C_{20}H_{2T}NO_4$, hydroberberin; a dilute solution of iodine in iodide of potassium precipitates the alcoholic solutions of the salts of berberine, producing green, mother-of-pearl-like, shining, scaly crystals, which resemble chrysanilin, and, like that, fix upon fibres without the use of mordants.

The root and concentrated liquid extracts of barberry are employed for

dyeing silk yellow; the colour produced is pure. Alum is added to the decoction of the root in the dye-beck.

Yellow Colouring Matters contained in Flowers.

Frémy and Cloëz have studied the yellow colouring matters contained in the petals of flowers, and have found that they contain two pigments, viz., xanthein, soluble in water, and xanthin, insoluble: the last-named substance is best obtained from the petals of the sunflower (Helianthus annuus), which are exhausted with boiling alcohol, from which, on cooling, is deposited the yellow pigment mixed with fatty matters, which latter are removed by saponification. The soap having been decomposed by an acid, the yellow fatty acid is exhausted with cold alcohol, leaving the xanthin as a residue.

Xanthin is an amorphous resinous body, soluble in alcohol and ether, and

probably identical with the pseudocurcumin of M. Schlumberger.

Xanthein, very soluble in water, is readily obtained from yellow dahlia flowers, which for this purpose are first exhausted with alcohol, evaporated to dryness, and the residue taken up with absolute alcohol. This solution is first diluted with water, next precipitated with acetate of lead, the ensuing precipitate suspended in water, decomposed by dilute sulphuric acid, the sulphate of lead removed by filtration, and the liquid evaporated to dryness. The xanthein thus prepared is readily soluble in water, alcohol, and ether; alkalies turn the colour a deep brown, but acids restore the yellow again. Xanthein yields coloured lakes with most of the metallic oxides, and dyes bright yellow shades on tissues.

M. E. Schwartz has tried several dyeing experiments with various vegetable products,—among these the blossoms of potatoes, lime-tree leaves and flowers, willow, poplar, horse-chestnut, oak, and other leaves,—with the view to ascertain whether these substances might answer as yellow dyes with aluminous mordants, but the results were not encouraging. The finest colours, and also the richest as regards yield of pigment, were horse-chestnut leaves and potato blossom (flowers of Solanum tuberosum); walnut leaves yield an orange-vellow.

It should be observed that there exist, in almost all parts of Europe, a large number of plants, the bloom or flowers of which contain a sufficient quantity of yellow colouring matter to be used for dyeing purposes, especially for olive colours; as an instance we name sage (Salvia colorans).

Carotin, Yellow Colouring Matter of Carrot Roots (Daucus Carota).

This dye has been investigated by Robiquet, Regnault, Zeise, and Husemann. The latter prepares carotin by exhausting the previously pulped and rasped root with water; the liquid is precipitated by tannin and a small quantity of sulphuric acid; the ensuing pasty precipitate is filtered, washed, pressed, and next exhausted with boiling alcohol at 80 per cent, which takes up mannite and a white-coloured substance, hydrocarotin, C₁₈H₃₀O. The residue, insoluble in alcohol, is treated with sulphide of carbon, the ensuing solution evaporated, and the dry residue treated with absolute alcohol. This solution yields, on concentration, a precipitate of carotin as a brown-red, crystalline, bulky substance, with a metallic reflex. It is soluble in benzol and sulphide of carbon, but insoluble in water and alcohol. This body becomes

decolourised by exposure to light, and also by the action of heat. Sulphuric acid dissolves carotin, forming a violet solution; sulphurous acid colours carotin indigo-blue. Formula, $C_{18}H_{24}O$.

Purrhee, or Indian Yellow.

Purrhee has been of late years imported into Europe, chiefly from India and China. It appears to be of animal origin, and to consist of intestinal concretions or urinary calculi, or deposits from the camel, elephant, and buffalo.

Purrhee is partly soluble in water, and is, on nearer investigation, found to be the magnesia-salt of a yellow-coloured sparingly soluble acid, named euxanthic acid, which may be prepared by first washing the dye-stuff with hot water; the residue (euxanthate of magnesia) is dissolved in dilute boiling hydrochloric acid, from which, on cooling, the euxanthic acid crystallises in needle-shaped crystals; sparingly soluble in cold, more readily in hot, water, also in hot alcohol, from which the acid is deposited again on cooling.

The formula of this acid is $C_{21}H_{18}O_{11}$. By dry distillation, and also by the action of strong sulphuric acid, it is converted into euxanthon, $C_{20}H_{12}O_6$, a yellow substance, sublimable in needle-shaped crystals; sparingly soluble in cold water and alcohol, but more so in the latter liquid when boiling.

Cotton, previously mordanted with alumina, is dyed yellow in a bath made up with purrhee water and borax or sal-ammoniac; silk is dyed yellow when immersed into a solution of purrhee in borax, the colour obtained being sulphur-yellow. Euxanthate of magnesia (i.e., the main constituent of purrhee) may also be decomposed by nitric acid not used in excess, and the aqueous solution of that fluid may be applied in the dye-beck without the addition of other substances: the colour thus obtained is apricot-yellow.

Yellow Colouring Matters of the Lichens.

Chrysophanic, Vulpic (Chrysopicric), and Usnic Acids.—We have already seen that some kinds of lichens contain colourless acids, capable of yielding, under the joint influences of ammonia and air, coloured substances. Other kinds of lichen contain ready-formed yellow dyes. Herberger, Rochleder. and Heldt, have extracted from the wall lichen (Parmelia parietina) a yellow acid (chrysophanic), largely found in the rhubarb root (Rheum palmatum), and in the Rumex patientiæ and Rumex obtusifolius; and Dr. Stein has obtained from the lichen just named a yellow principle (chrysopicrin) identical with vulpic acid, obtained by Mueller and Strecker from a variety of Norwegian lichens (Citraria vulpina, Evernia vulpina), and by MM. Bolley and Kinkelyn, the Evernia vulpina from the Alps. Usnic acid-found by MM. Knop, Rochleder, and Heldt, in the Usnea florida, Usnea hirta, Usnea plicata, Usnea barbata, Cladonia rangiferina, Parmelia purpuracea, and Ramolina calicaris -completes the list of the yellow substances produced by lichens, all of which have great similarity with each other. The yellow-coloured matter found by M. Picard* in the leaf-buds of the poplar tree (Populus nigra, Populus pyramidalis), and named chrysinic acid, approaches vulpic acid.

Since the yellow-coloured acids of the lichens are scarcely soluble in water, but readily soluble in alcohol, ether, and alkaline solutions, from which these acids may be obtained in a crystalline state, the process of extraction from the

^{* &}quot;Journal für Praktische Chemie," xciii., 369.

raw material cannot be difficult. The lichens are best treated with an alkaline lye, and then precipitated by an acid; the precipitate thus obtained is dissolved

in alcohol or ether, and these solutions left to crystallise.

Chrysophanic, Rumicinic, or Rhubarbaric Acid, also called Lapathin.* -Formula, C10H8O3. Yellow needle-shaped crystals, which turn red by the action of nitric acid, and dissolve in concentrated sulphuric acid, yielding a red solution. It also dissolves in caustic potassa, yielding likewise a red liquid, which on evaporation deposits a blue flocculent matter, soluble in water, and then again producing a red solution. This acid is decomposed when strongly heated, yielding a yellow flocculent sublimate.

Vulpic Acid.—Chrysopicrin, scarcely soluble in water, either hot or cold; soluble in 588 parts of cold and 88.3 parts of boiling alcohol, and soluble in ether; fuses at 110°; sublimes at 120°; the sublimate forms brilliant goldenyellow, scaly particles, soluble in alkaline liquids. This solution is not acted upon by air; when treated with hypochlorite of lime it yields an oily liquid and a red resin. This acid does not yield good results in dyeing.

Usnic Acid is a scaly, crystalline yellow substance, insoluble in water, sparingly soluble in boiling alcohol, soluble in ether and alkalies. These lastnamed solutions become carmine, and at last black, on exposure to air. If submitted to dry distillation this substance yields beta orcin.

Chrysinic Acid above mentioned is of no importance at all, and hitherto none of these substance have been applied industrially.

Gentianic Acid.—The well-known gentian root contains a vellow acid. forming needle-shaped crystals, sparingly soluble in water, more readily so in alcohol and ether; with alkalies it yields golden-yellow crystallisable salts; nitric acid converts it into a green insoluble substance, which appears to be nitro-gentianic acid.

Annatto, or Anotto, also known as Rocon, Bixin, or Orleans.

Annatto is mainly the pulp which surrounds the fruit of the Bixa orellana, a shrub native of South America, and cultivated in Mexico, Brazil, Guiana, and the Antilles. When the fruit has reached maturity the fruits are gathered, the seeds pulled from the capsules and coarsely pounded up with the pulp while placed in water, and left to ferment for several weeks. After this time the pulp and liquid are passed through a sieve; the colouring matter soon settles to the bottom of the liquid, and having been collected is evaporated by heat, put in boxes, and dried in the sun.

Annatto is imported into Europe in the shape of cakes, weighing from 5 to 8 kilos., packed in banana leaves (Guiana anotto), or as cakes packed in casks (from Brazil), or in tinned iron boxes from Cayenne. This latter kind is about twice as rich in colouring matter as the ordinary annatto of commerce; its colour is bright, its smell pleasant; it contains about 5 per cent of mineral matter, and from 67 to 70 of water. † It has been regularly manufactured at Cayenne since 1837 by M. Daubriac.

In the year 1848 Dumontal introduced an improved mode of preparation of

* "Annalen der Chemie," cvii., 324. "Répertoire de Chimie Pure," iv., 371. "Journal für Prakt. Chemie," lxxxiv., 436.

^{+ &}quot;Girardin, "Mémoire sur la Bixin." "Journ. de Pharm. et de Chimie," xxi. 174 [3]. Girardin, "Mémoire sur la Falsification du Rocon." "Journal de Pharmacie, Cahier de Mars," 1836.

annatto, whereby the fermentation is evaded, and the pulp simply washed out from the capsules, and off the seeds. In this way a product is obtained from five to six times more valuable than the ordinary annatto, and the product has become known as bixin, since it yields better and purer shades. The ordinary annatto of commerce is a homogeneous unctuous paste, of a dull yellowish red externally, more bright internally, and giving off a disagreeable urinous smell. It contains on an average-Water, 72 per cent; leaves and other foreign organic matters, 22 per cent; colouring matter, 6 per cent. The annatto as usually met with in trade is frequently adulterated, either designedly, or by ignorant preparation, with red- or yellow-coloured mineral matters, as ochre, colcothar, ground-up bricks. These impurities are detected by drying the substance first at 100°, and then igniting it in a platinum crucible. Annatto of good quality does not yield more than from 8 to 13 per cent of ash, of a yellowish colour. As regards the quantity of real colouring matter contained in annatto, this varies according to the quantity of water present, which is estimated by drying at 100° about 10 grms. of the substance. The colouring matter is estimated by a dyeing process, for which M. Girardin gives the following instructions:-For cotton he takes of previously dried (at 100°) and ground annatto, 5 grms.; carbonate of potassa, 10 grms.; water, 400 grms. For silk-Annatto, 0.5 grm.; carbonate of potassa, 1 grm.; water, 200 grms. The mixture is heated to boiling, along with 12 grms. of cotton-thread or yarn, or 2 grms, of skein silk; the ebullition is continued for fifteen minutes; the vessel is then removed from the source of heat, and left standing for an hour; the yarn is then taken out, squeezed, and dried in the shade. This assay is made in comparison with a standard sample.

The colouring matters of annatto have been investigated by Chevreul,* Bousingault,† Kernot,‡ Picard,|| Bolley, and Mylius§. When treated with water, annatto yields a yellow colouring matter, soluble in water and alcohol, insoluble in ether, and capable of imparting a yellow colour to tissues previously mordanted with alum. The colour has been named orellin. The residue, after exhausting the annatto with water, contains its chief colouring matter, bixin, which may be obtained, according to Bolley, as follows:—Cayenne annatto is first washed with water and dried, next exhausted with very strong boiling alcohol; the tincure is filtered, and then evaporated on a water-bath; the residue digested with ether, which dissolves a portion thereof, leaving a cinnabar-red powder, fusible at 100°, soluble in alcohol, but insoluble in water; not affected by a heat of 145°, nor by boiling with dilute sulphuric acid, soluble in weak alkaline solutions, and in soap-water, exhibiting a yellow or orange-yellow colour. According to Dr. Bolley, the formula of this substance is C5H6O2; the matter soluble in ether has not been further investigated.

According to Kerndt, there is left on the evaporation of the ethereal solution a substance which fuses at 100°, and the formula of which should be $C_{12}H_{22}O$. Picard considers this to be an error, stating that the product is a mixture of substances, including fatty matters. The impure bixin (obtained as above

^{* &}quot;Leçons de Chimie Appliquée à la Teinture.

^{† &}quot;Annales de Chimie et de Physique [2], xxviii., 440.

t "Jahresbericht der Reinen und Angewandten Chemie," &c., by Liebig and Kopp, 1849, p. 457

[#] Schweitzerische, "Polytechnische Zeitschrift," 1861. "Répert. de Chimie Appliquée," 1861, 419.

[§] Schweitzerische, "Polytechnische Zeitschrift," ix., 134

described) is first dissolved in alcohol, soda solution is next added, and the alcohol distilled off; the liquid is then shaken up with ether, which extracts a soft fatty matter, and afterwards treated with carbonic acid, whereby a sodasoap is precipitated. Acetic acid is then added to neutralise the alkali, and the ensuing precipitate of organic matter is treated with ether, which, on evaporation, yields an amorphous blood-red pulverulent substance, sparingly soluble in ether and alcohol when cold, but soluble in boiling alcohol and in benzol. As this substance is not fusible at 100°, orellin is, according to Dr. Kerndt, derived from bixin, by having become altered by the action of air and water. Concentrated sulphuric acid dissolves bixin as well as annatto, yielding a deep blue-coloured liquid. From these particulars it will be evident that the chemical history of annatto is very incomplete.

Annatto is used in dyeing and printing tissues, and for colouring oils, grease, butter, cheese, and varnishes. The shades yielded by annatto upon tissues are bright, and resist the action of acids and soap; but though even chlorine scarcely affects this dye, it fades on exposure to light and air. When annatto is used alone it yields bright orange-red or orange-yellow colours, and it is sometimes used to enhance the brightness of other dyes which produce red, yellow, orange, or pink. In order to dye cotton with this ware it is first dissolved in carbonate of potassa or soda, the liquor boiled, or in some instances (according to the nature of the fabric) heated to 60°; the goods dyed are left in the bath for a quarter of an hour, after which they are pressed out, and washed in slightly acidified water. Better results are, however, obtained by first mordanting with stannate of soda and sumach, and by nearly neutralising the alkaline bath with sulphuric acid, so as to prevent the precipitation of the colouring matter, and yet keep the the latter quite ready to become fixed immediately on the fibre. For printing on cloth a solution of annatto in caustic potassa is used, the tissue next aged, and then placed in either a weak acid bath or in a weak solution of alum or chloride of tin. For steam colours the following mixture may be used:-

Caustic soda solution (sp. gr. 1.086, containing) 8 litres 6 litres about 7.8 per cent of actual soda 5 kilos. Annatto paste 750 grms. Boil for ten minutes, and add next of-Tartaric acid 90 grms. 70 grms. . . I kilo. Alum 350 ,,

These preparations are thickened with gum or farina water, and next printed, steamed, and washed. Silk requires no mordant for dyeing with annatto; the bath is made up of equal parts of annatto and crystallised carbonate of soda, to which sometimes soap is added; the temperature is 50°, and the silk is worked for a quarter of an hour. The reddish yellow or deep orange shade is rendered yellow-orange by rinsing the fabric through lemon-juice or a weak solution of tartaric acid.

Green Colouring Matters.

Chinese Green. Lo-kao.*—During the first portion of the year 1848 D. Keechlin-Schouch found, while examining some cotton cloth brought from

^{*} Dingler's "Polytechn. Journ.," cxxvi., 238; cxlvi.; cxlix., 140; clxv., 397. "Comptes Rendus de l'Académie des Sciences," xxxv., 558. "Bulletins de la Sociéte d'Encouragement,"

China a few years previously, that it had been dyed green by a substance unknown in Europe.* A piece of this cloth having been sent to M. Persoz for investigation, he found that the dye was of organic origin, and quite different from any then known in Europe. The first genuine sample of the dye-ware ever sent to Europe was received by M. Persoz,† through the kindness of M. Forbes, then United States Consul at Canton. Shortly after this sample had been sent to Paris a comparatively large quantity of lo-kao came via Batavia to Holland, and having attracted the attention of the silk dyers at Lyons, was sold at 533 francs per kilo.

Lo-kao is met with in commerce, or rather was, since it is now-a-days almost entirely superseded by the aniline greens, in the shape of thin laminæ, varying in thickness of from I to 4 millimetres, and from 2 to 5 centimetres square. These laminæ exhibit a blue colour, with a violaceous or green reflection; they are fragile, yet difficult to pulverise, becoming a pasty mass. Lo-kao contains from 21.5 to 33 per cent of ash, chiefly oxide of iron, lime, and alumina; 9.3 per cent of water; and 61.9 per cent of colouring matter. It is decomposed by heat, but does not yield any sublimate; it is insoluble in alcohol, wood-spirit, sulphide of carbon, and ether. Water does not dissolve lo-kao, but makes it swell up; dilute and cold acetic, hydrochloric, sulphuric, and tartaric acids aid its solution. With the aid of heat the solutions of lo-kao are rendered olive-brown by concentrated acids, an iron-grey precipitate being deposited, and the supernatant liquid becomes yellow, and turns orange on the addition of an alkali. Concentrated sulphuric acid dissolves lo-kao, yielding a reddish brown solution.

Alkalies at first aid the dissolution of this green pigment, but when it is left a long time in contact with the alkaline fluid the colour turns brown, and more rapidly at a boiling temperature, being converted into a new pigment, which cannot be again made green, but which has the property of becoming fixed upon previously mordanted cotton. The alkaline carbonates also destroy the green colour on prolonged action along with water at a pressure of from 2 to 3 atmospheres.

The reducing acids, such as phosphorous, arsenious, hyposulphurous, oxalic, and formic, when added to lo-kao, cause the formation of a purple-violet precipitate. Hydrosulphuric acid converts lo-kao and its solutions into a blood-red substance, but by the action of air the liquid becomes gradually green again, after having passed through a series of intermediate shades. Hydrosulphuret of ammonia also reduces and energetically dissolves lo-kao. Protochloride of tin dissolves lo-kao largely, and turns its colour blood-red.

liv., 415; lv., 290. "Répertoire de Chimie Appliquée," l., 11, 75, 78, 370; ii., 53; iv., 405. Buchner's "Repertorium," viii., 69. "Bulletin de la Société Industrielle de Mulhouse," xxv., 96. "Notice du Vert de Chine et de la Teinture en Vert chez les Chinois," par M. Natalis Rondot; suivie d'une "Etude des Propriétés Chimiques et Tinctoriales du Lo-kao," par M. J. Persoz; et de "Recherches sur la Matière Colorante des Nerpruns Indigènes," par M. A. F. Michel. Paris: chez Lahure et Co., 1858.

^{*} Letter from the Chamber of Commerce of Mulhouse to the then Minister of Commerce, &c., viz., M. Dumas, 27th April, 1850.

[†] This is the statement as found in the published papers above quoted, but from a private communication we know with perfect certainty that a sample of the dye was brought over along with the cloth.

The primitive green colour is, however, restored by the addition of an alkaline acetate, or of a strong base and simultaneous exposure to air.

Oxidising agents, such as nitric, chloric, iodic, and chromic acids, destroy the Chinese green, the ultimate result being the formation of a red substance different from that which is formed from the lo-kao by reducing agents, since the latter is capable of being re-converted into the original green colour. Some salts, among which are alkaline phosphates, pyrophosphates, borates, margarates, oleates, and stearates, assist the solution of lo-kao in water, while the salts of magnesia and zinc turn its colour to a pure blue; nitrate of silver and ferricyanide of potassium oxidise the colouring matter if an alkali is simultaneously present. Lo-kao possesses the peculiar property of so masking the presence of certain bases, e.g., lime, oxide of iron, and others, that they can only be detected after the complete destruction of the organic matter by incineration. The opinion of M. Persoz on lo-kao is, that it is a mixture of lime, magnesia, and iron-lakes, along with some phosphate of alumina, and partly soluble in water. He gave the name of cyanin to the pure colouring matter, freed as much as possible from the accompanying inorganic substances. It has a blue colour, and contains no nitrogen.

Persoz gives the following directions for the purification of the commercial article:—(1). Lo-kao is dissolved in a saturated solution of carbonate of potassa; after the liquid has lost its turbidity, water is added to the previously decanted clear liquid; after a while there is formed a green precipitate, which, after being washed and drained, may be successfully used for dyeing and printing.
(2). Lo-kao is first soaked in water, and after it is swollen and softened it is mixed with one-and-a-half times its weight of acetic acid; next 5½ parts of water are added, the liquid filtered, and to the filtrate ammonia is added, whereby a lake far richer than the original substance is obtained.

An aluminous lake may be obtained when a solution of lo-kao, to which an alum solution is added, is precipitated by an alkaline carbonate, or also by the addition of a salt of alumina to a solution of lo-kao in carbonate of soda. The double chloride of ammonium and tin yields, with an aqueous or acetic acid solution of lo-kao, a beautiful blue precipitate if care be taken to add acetate of soda at the same time. The purple-violet precipitate obtained by the action of the reducing acids, such as arsenious and formic, is soluble in acetate of lime, and that solution deposits after some time a deep blue powder, verging upon violet.

As regards the origin and mode of preparation of lo-kao, the results of the researches made in China by Father Hélot, by MM. Montigny, Edan, Arnaudtizon, Fortune, Rémi, Edkins, and others, coupled with the botanical investigations of samples of plants sent over to M. Decaisne, prove that lo-kao requires for its preparation two different plants, viz., the Rhamnus utilis, called in the Chinese language, hong-pi-lo-chou, and the Rhamnus chlorophorus, pé-pi-lo-chou. One of these shrubs grows wild, while the other is purposely cultivated, but which of the two is not known with certainty. The hong-pi-lo-chou, also known as hom-bi-lo-za, is said to yield by itself a deep and fast colour, but void of brilliancy, while the pé-pi-lo-chou yields a weak but brilliant colour. In order to render the mode of preparation of lo-kao in China properly understood, we have first to describe the mode of dyeing the cloth by means of the vegetable matters in question, the lo-kao being obtained by detaching from cloth the excess of colour fixed thereupon.

The following is the descripition of the process as carried out at A-zé, and witnessed by Hélot:-The fresh (green) bark of the hong-pi-lo-chou is first boiled with water, and left standing in that liquid for two days; the preparation of the infusion of the green bark of the pé-pi-lo-chou lasts for ten days. Each of these infusions is separately employed, and when used lime-water is added. The cloth is first dipped from seven to ten times in the hong-pi bath, and next three times in the pé-pi bath, but the fabric is dried after each separate immersion. This drying is effected in meadows, where the cloth is spread out at about nightfall, and left until noon the next day, the action of the sun being indispensable for the development of the colour, only the side of the cloth exposed to the sun's rays being dyed. It is a remarkable fact that this Chinese cloth thus green-dyed is very intensely coloured on one side, and only faintly so on the other. This appearance induced Persoz to doubt the correctness of Hélot's statement, Persoz expressing himself on this matter as follows: - Since the Chinese green-dyed fabrics have a right and wrong side, they cannot have been dyed by immersion, but the dye has evidently been imparted to the cloth either by a brush or other mechanical means; while, moreover, the change which the colour undergoes by exposure to the sun's rays proves that the dye has not been imparted in the way described by Hélot.

The researches, however, of M. Michel on indigenous European plants of the same genus as those used in China clear up this subject, as we shall see presently. The cloth dyed as above described, having become quite dry, is placed in cold water, and thoroughly washed and rinsed through; the washwaters are collected together, poured in a large cauldron, and the water is boiled after there has first spread over its surface a tight network of cotton yarn, upon which the colouring matter is deposited during the process of ebullition. In order to collect a quantity of the colouring matter, this process of ebullition has to be repeated with fresh quantities of water wherein the previously dyed cloth has been washed. When the cotton yarn is sufficiently charged with pigment the former is washed in cold water, and well rubbed with the hands, by which means the lo-kao becomes detached, and slowly settles in the water; the precipitate is washed by decantation, and the thin pasty mass of pigment is placed upon paper, and dried by first absorbing a portion of the moisture by means of ashes, and next dried in the sun. The layer of lo-kao while drying becomes detached from the paper, and by the latter being bent the pigment presents the aspect of the irregularly shaped, small, thin, yet hard laminæ as met with in commerce. The weight of cotton yarn required to exhaust the pigment from 300 pieces of dyed cloth, the length of these pieces not being mentioned, is 3.62 kilos. In order to obtain the weight of 1 kilo. of lo-kao, 1060 pieces of dyed cloth are required, and since, according to the statements of Hélot, the five manufactories of lo-kao at A-zé cannot annually yield more than from 18 to 24 kilos. of lo-kao, the high price of that substance is readily explained.

M. Michel, at Lyons, has experimented with the bark of the *Rhamnus catharticus*, following the same mode of operation as that described,—that is to say, placing cloth in aqueous infusions of the bark, and repeating these dippings, each being followed by a drying of the cloth by exposure upon grass during the night and a portion of the daytime: he obtained a rather intensely

violet-coloured cloth, which turned green on being washed in a boiling dilute solution of alum. The green dye thus obtained lacked the brilliancy and intensity of the Chinese dyed cloth, but the reactions were the same, and, moreover, the cloth prepared by M. Michel had a wrong and right side, just as described for the Chinese cloth. The cloth dyed by M. Michel had its right side there where it had been exposed to diffused light. There does exist, therefore, in the Rhamnaceæ a peculiar substance, not yet isolated, which has the preperty of becoming green under the influence of the white diffuse light of the sky.

Green Dyeing.

The Chinese dye the woven tissues or yarns green either by making use of the barks already mentioned, in which case the dyed fabric has—as regards the colour—a right and wrong side, or they use the lo-kao, in which latter case both sides of the cloth are dyed alike: this difference is readily explained by the researches of M. Michel, because, as regards the first case, there is fixed on the cloth a colourless but colourable matter, which does not develope its colour but when exposed towards the light; in the second case, there is used a ready-formed pigment.

When the dyer desires to use the bark only, the following processes are used:

- a. Process of Khiu-tchéou-fou.—The fresh bark of pé-pi-lo-chou is boiled, and to every 100 kilos. of the liquid are added 63 grms. of Chinese potash; the cloth is immersed in the liquid from two to three times, and dried in the sun after immersion. At Chan-toung alum is used instead of potash.
- b. Process of Emou-i, as described by Mr. Sinclair.—The bark of lo-tsé* is placed in hot water, and next boiled for an hour; potash and alum are added; the liquid is next decanted and filtered, and left standing over night; the goods are next immersed in the bath, and after that dried by exposure to open air, the pieces being stretched out over the grass, but only during the earlier hours of the day. This dyeing and drying operation has to be repeated several times before the desired shade of colour is obtained.

Lo-kao is not used in China even for dyeing more common and coarse kinds of cotton goods, but only for bright colours. The pigment is dissolved in a hot solution of potassa, and the previously well-washed cloth is immersed in this bath, kept at a temperature of 50° or 60°. Immediately after the first immersion the goods are wrung out by mechanical means, and the dyeing operation is repeated a second time, again followed by wringing out, and next a washing in fresh water and drying in the open air, which ends the proceedings. There is not the least doubt that the Chinese use lo-kao for silk-dyeing, and also apply the *Rhamnus* barks for that purpose, but their process of operating is unknown.

The researches of Stanislas Julien, who was a resident in China for many years, have proved that the use of the lo-kao and the bark from which it is

^{*} Although this word differs from that mentioned under a, the material is no doubt the same, it being a well-known fact that there are very many dialects in use in China, the extent of that country exceeding by one-third that of the United States of America, which measure fully 3,500,000 square miles.

obtained has only been known to the Chinese themselves since about thirty-five years. It is quite certain, also, that no mention whatever is made of Chinese green and the use of the barks, for any purpose whatever, in the otherwise very-correctly written and published Chinese books on botany and agriculture issued about the middle of the last century.

French Process for Dyeing with Lo-kao.

E. Michel, at Lyons, dyes silk green (Vert-Venus, Vert-Azof, or Vert-Lumière, the latter appellation being given because this green colour does not appear blue when seen in artificial light) by soaking in an aqueous solution of alum (sp. gr. 1.034), for three days, a quantity of 5 grms. of lo-kao and 30 grms. of the solution just alluded to. The pigment is next thoroughly incorporated with the solution of alum by stirring and rubbing with a glass rod, while the fluid is simultaneously diluted by the addition of 250 grms, of the alum solution; the liquid is left again standing for twenty-four hours, and then carefully decanted from any sediment. The colour of this fluid is very deep green, nearly black. This operation is repeated with a fresh quantity of pigment, so as to obtain at least a litre of the solution, which keeps very well. M. Michel found that if to this solution of lo-kao a sufficient quantity of spring water were added, containing lime salts, there ensues gradually a precipitate of a calcareo-aluminous lake, and he contrived to find, by a series of experiments, what quantity of such spring water would be required for obtaining a fluid from which this lake did not precipitate immediately, or even after a length of time, but which yet possessed the property of depositing the colouring matter it contains on the fibre of textile fabrics when they come into contact with it. The quantity of spring water at Lyons required for I litre of lo-kao solution was found to be 15 litres; in a solution of that description silk was dyed without any other precaution than a slight deviation of temperature, and the depth of the shade is regulated by the number of repeated immersions. He found that, in consequence of the various operations silk is submitted to before being dyed, it contains a small quantity of lime-salts, which act in this case as a mordant; but in some cases the silk might advantageously be immersed in spring water containing lime before the dyeing process. Instead of using the lo-kao of commerce, it is preferable to apply it in the purified state prepared according to the method of M. Persoz, described above.

The following is another method for dyeing with lo-kao, suggested by Persoz:—The lo-kao is dissolved in a moderately strong and slightly acidulated solution of tin-salt, and the silk is immersed in this liquid and kept at the ordinary temperature: it assumes a pale salmon-colour, and is next washed in a liquor made up of ammonia, potassa, or acetate of lime. The colour thereby becomes first purple, and next blue, and the blue is converted into green by dyeing in a cold infusion of Persian berries: the silk may, if preferred, be aluminised first, and next put into a solution of lo-kao in sulphydrate of ammonia. After the immersion of the silk in this liquor it is thoroughly aged, and in order to obtain the requisite depth of shade the immersion is repeated once, twice, or oftener. The lo-kao may also be first steeped in a weak alkaline lye, and next saturated with hydrated protoxide of tin; the silk is placed in this solution, and the fabric exposed to air, when it

turns blue by the oxidising action of the atmosphere, and is converted into green by a yellow dye.

According to M. Persoz's opinion, the Chinese green-dyed cotton is, like all greens of organic origin (excepting aniline green), the result of a combination of blue and yellow, and he also thinks that there is no ground at all for supposing that the green dye imparted to cotton in China and the pigment known as lo-kao are identical, because in the former the yellow, and in the latter the blue, predominates. This opinion is strengthened by the fact that the process of dyeing of M. Michel produces upon silk a colour which is a bluish-green, and only by the aid of picric acid can this be converted into a pure green.

If desired to dye cotton a green with lo-kao the following process is recommended by M. Persoz:—From 50 to 60 grms. of white soap are dissolved in to litres of water, to which is added a sufficient quantity of lo-kao, previously steeped and consequently swollen in water, or, better yet, the purified pigment. The liquid so obtained is heated, and the cotton, on immersion, is at once dyed.

For the purposes of printing the cotton fabric may be alumed first, but this is not indispensable. The colour consists of gum-water wherein lo-kao, previously steeped and swollen up, is finely divided, or an aluminous lake may be used, with or without the addition of acetate of alumina. Another plan is to print on a thickened solution of lo-kao in tin-salt: after drying, the fabric is passed through a solution of acetate of lime, to which an excess of lime is added. Cotton may be dyed, also, with a solution of lo-kao in sulphydrate of ammonia, followed by a well-conducted exposure to air.

M. Persoz has succeeded in fixing lo-kao on woollen fabrics by preparing first a tin lake of that pigment: this lake is suspended in water, which is next heated, and the wool being entered, and some drops of a solution of oxalic acid added, it becomes perfectly dyed. The same lake may be thickened with gum-water acidulated with oxalic acid, and printed on to woollens and worsteds, yielding, after steaming, a beautifully green colour.

The beautiful shades of green as obtained from lo-kao have almost disappeared from the market, first, from their want of stability, and, secondly,

because of the discovery of the coal-tar colours.

Lo-kao is also noticeable as being the only substance we are acquainted with capable, with proper reagents, of producing all the seven colours of the spectrum. Though driven from the market, it remains an interesting substance.

It is an interesting fact, that while the greens produced by indigo and picric acid appear blue in artificial light, those produced with Prussian blue and picric acid appear green under the same conditions.

Other Green Dyes of Vegetable Origin.

We will now briefly notice some green pigments and dyes which have been noticed, but are, after all, very little known in Europe, and which may be identical with or analogous to Chinese green.

M. Poivre, French Minister-Plenipotentiary in Cochin China (1749), and Father Horta, who visited that country as a missionary (1766), speak of a plant called *Tsaï*, which was cultivated in Cochin China and neighbouring countries, and which plant, on being fermented, as indigo usually is, produced by that

process a mealy green substance, which yielded by itself an emerald-green on cloth. Since that period nothing further has been learned on this substance, nor of the plant, but there is no reason at all to doubt the statements of the two travellers above named.

Dinh-schan, also belonging to Cochin China, is noticed by M. Charpentier de Cossigny, who resided there (1770), in the following terms:—The natives of this country have a plant which they call dina-schan, and which bears some resemblance to our Melissa: from that plant they obtain, by macerating it in water, a green mealy substance, which is used by them for dyeing all kinds of fabrics different shades of green. It is not unlikely that the pigment here alluded to is the tsai above mentioned, and the plant from which it is obtained is either the Mercurialis perennis, or, perhaps more correctly, as stated by the Jesuit Correa, the Justicia tinctoria, belonging to the natural order of the Acantheæ.

Green Indigo may be obtained, according to M. Charpentier de Cossigny, from the Indigofera tinctoria, by steeping the leaves of that plant for some time in fresh water, or in weak milk of lime for an hour only, and then pressing the leaves and repeating the steeping process, with a fresh quantity of water, for another hour: the two liquids thus obtained are poured together and filtered; lime-water is added. The filtrate is vigorously stirred about, depositing a green mealy substance, which is first washed with lime-water, and next with fresh water. The green indigo brought over from India in 1790, by Prinsep, appears to have been, according to the statements and researches of Bancroft, a substance analogous to chlorophyl, soluble in alcohol, and mixed with some ordinary indigo.

Barasat Green was in 1793 imported from Calcutta in very small parcels, said to be obtained from the Asclepias tinctoria, but in the opinion of M. Persoz this substance is merely an impure and immature indigo. The same observation applies to the green indigo investigated by M. Kurer (1801), and to the vegetable green sent from China and Java by M. Cézard (1837).* This substance was analysed by M. Schwartz, and found to contain, in 100 parts—Yellow colouring matter, 10:40; gluten and salts, 35:30; indigo-brown, 39:20; mucilaginous matter, 5:10; indigo-blue, 10:0.

The substance known in China as Whi-mei, and exhibited at the London Exhibition of 1851, is the product-of the Sophora Japonica, the bloom of which is called Hoai-hoa, and used as a green dye.

Chlorophyl; Chromule; Green Colouring Matter of Leaves and other Green Parts of Plants.

The green colouring matter or pigment widely diffused through the vegetable kingdom is, notwithstanding the many researches made by different authors, as yet only imperfectly known. Some investigators consider it as a green principle, while others, and among them M. Frémy, state that it is a mixture of a yellow matter (phylloxanthin) and a blue pigment (phyllocymin), but the chemical reagents used for the separation of the two supposed pigments are powerful enough to cause the probable decomposition of a substance so readily altered as chlorophyl.

M. Verdeil isolates the chlorophyl by exhausting the plant or leaves with

^{* &}quot;Bulletin de la Société Industrielle de Mulhouse," xi., 27.

alcohol; the solution is precipitated with lime, and the lime lake thus produced is washed, and next decomposed by hydrochloric acid; the acid solution is shaken up with ether, which takes up the green pigment. On evaporating the ether the pure chlorophyl is left. The chlorophyl thus obtained is a deep green powder, unacted upon by exposure to air, not decomposed at 200°, and not fusible at that temperature; insoluble in water, but soluble in alcohol, ether, acids, and alkalies: hydrate of alumina combines with this pigment, and withdraws it readily from its alcoholic solution provided it be first properly diluted with water.

Nascent hydrogen reduces and decolourises chlorophyl, which, according to M. Verdeil, contains a large quantity of iron in a peculiar state of organic combination analogous to the state iron is found in the hæmatin (red colouring matter of blood).

According to Dr. G. J. Mulder, chlorophyl should contain nitrogen, but it is presumable that the chlorophyl he prepared from grass was not sufficiently purified, and therefore contained some protein compound. When an alcoholic solution of chlorophyl is first diluted with water, and next treated with gelatinous alumina, there is formed a deep green lake, while the supernatant liquid becomes yellow. This experiment has suggested to M. Frémy the idea above alluded to, and the following plan of separating the supposed pigments:—First, a saturated solution of hydrochloric acid in ether is made, by mixing in a glass stoppered bettle 2 parts of ether and 1 part of hydrochloric acid, slightly diluted with water; the acid is made to saturate the ether by strongly shaking the bottle containing the mixture: on the other hand, the chlorophyl is treated with an alkali, whereby it is converted into a beautiful yellow body, soluble in alcohol, ether, sulphide of carbon, and capable of forming with hydrate of alumina a yellow lake, which, on being decomposed by means of an acid, gives up its pigmentary matter to any of the solvents just named.

When the yellow pigment just mentioned is treated with the mixture of hydrochloric acid and ether the latter fluid becomes purely yellow, while the lower layer of hydrochloric acid assumes a beautifully blue tint. The explanation of this phenomenon is given by M. Frémy in the following terms:—Chlorophyl, he says, is a mixture of a blue and a yellow pigment, the blue of which is temporarily bleached by alkalies, and the yellow pigment—which they produce from the originally green-coloured substance—is a mixture of the primitive yellow and the colourless product formed by the action of the alkalies upon the cyanin. When, therefore, the yellow matter is treated with ether and hydrochloric acid, the original yellow pigment of the chlorophyl is dissolved in the ether, and the cyanin, being restored to its colour by the acid, becomes dissolved in the latter, forming a blue solution. This experiment may be readily made, either with chlorophyl or with previously dried green leaves.

The name of phylloxanthin is given by M. Frémy to the supposed original yellow constituent of chlorophyl, while he calls the yellow substance resulting from the temporary alteration of the blue principle (phyllocyanin) contained in chlorophyl, phylloxanthein.

The regeneration of phyllocyanin by acids does not require the action of air. When plants are reared in the dark, or at least nearly so, direct sunlight being excluded, they contain phylloxanthin and phylloxanthein, and by the

action of acids the green colour is rapidly restored. The yellow leaves which fall in autumn contain phylloxanthin only, and their alcoholic extract does not yield—when treated with the above-named mixture of hydrochloric acid and ether—the characteristic phenomenon: the cause, therefore, of the autumnal change of the leaves is the fact that while the phylloxanthin—a rather stable compound—remains, the phylloxyanin is oxidised and completely decomposed. We mention these facts here because they give a clue to the failures of chlorophyl as a dye-ware.

It may interest our readers to learn what kind of attempts have been made, especially by M. Verdeil, to fix the green colouring matter of plants to woven textile fibres. He extracts from the fleshy parts of the immature flower-buds of the thistle and artichoke a green-coloured pigment, apparently different from chlorophyl as well as from lo-kao. The juice squeezed from the buds is originally colourless, but by the action of air and the addition of carbonate of soda it assumes a greenish-yellow, which is converted into a bluish-green after neutralising with acetic acid. The colouring matter is next precipitated by acetate of lead, and the ensuing precipitate is decomposed by means of sulphuric acid diluted with alcohol, and kept at a temperature of 40°. The alcoholic solution becomes yellowish-brown; the sulphate of lead having been removed by filtration, the colouring matter is precipitated by the addition of ether, and the precipitate, having been collected on a filter, is first washed with ether and next with water. The substance thus obtained is insoluble in water, ether, and acids, but soluble in alcohol and alkalies, forming, with the oxides of aluminium and tin, deep green lakes, which resist the action of light, and might be applied for the purposes of printing on tissues, as well as for artists' colours. The green is not, however, particularly beautiful.

M. Hartmann* has experimented for the purpose of applying the chlorophyl of grass to woven fabrics. This chlorophyl is prepared in the following manner;—The grass is first washed with warm and slightly alkaline water, and then steeped for twenty-fours in a caustic soda-lye of sp. gr. 1.070, containing about 7.75 per cent of dry caustic soda; the deeply coloured fluid is decanted, and next precipitated with hydrochloric acid, yielding a flocculent green matter, which is collected upon a filter and washed. The quantity of chlorophyl thus prepared is far from abundant, being only I part for 100 parts of grass. The pigment, suitably thickened with gum, to which lime-water or ammonia is added, yields, when printed and steamed, colours which—although not exactly beautiful—are fast, and prove, moreover, that chlorophyl may be fixed on woven fabrics.

M. Cordillot prefers the following process:—Grass is first exhausted by boiling water, and next treated with a very weak caustic soda solution (sp. gr. 1'013), which also contains some phosphates of alumina and lime; the previously decanted green liquid is neutralised with hydrochloric acid, whereby a green flocculent matter—a lake of chlorophyl—is thrown down.

For the purpose of printing the author takes 250 grms. of a caustic soda solution, sp. gr. 1'333, containing about 31'2 per cent of dry caustic soda to 1 kilo. of the moist pasty lake: this solution has a specific gravity = 1'070. 100 kilos. of grass yield about 8 litres of the pasty lake, which, after having

^{* &}quot;Bulletins de la Société Industrielle de Mulhouse," xxvi., 283.

been thickened with gum-water, is printed and steamed. The following substances may, if desired, be added to the lake:—Phosphate of soda, either alone or mixed with pasty hydrated binoxide of tin, binarseniate of potassa, alone or with the same preparation of tin.

When silk or wool is put in a bath made up of extract of chlorophyl (sp. gr. 1.070), and containing phosphate of soda and oxide of tin, very deep shades are produced.

It is a well-known fact that dead wood often exhibits a green colour: such wood yields, when treated with chloroform, a beautifully bluish-green matter, which differs from chlorophyl by its chemical properties, and has been named

xylochloric acid.* The flowers of the tree Sophora Japonica, a native of Japan and China, belonging to the Leguminoseæ, yield a yellow and green pigment, the former being, according to Dr. Stein, identical with the rutinic acid obtained from the flower-buds of the Capparis spinosa, and occurring in the Ruta graveolens. The yellow flowers of the tree known in China as hwae or hoar are collected just before they begin to fade, sun-dried, moistened with the juice of some other flowers which are pounded along with salt in a mortar, formed into the shape of small balls, and next gently dried in the shade. When it is desired to dye silk yellow by means of this preparation, the silk is first steeped for twelve hours in a solution of alum, and next placed in a boiling decoction of the hoar. MM. Michel and Guinon state that the colouring matter only exists in the flowers. Alkalies redden the pigment, acids discolour it; bichromate of potassa turns the colour a bright mahogany-brown. In order to dye green with this substance the Chinese make use of the action of sunlight: they immerse, according to the statement of M. Madows, the cotton in a boiling alumed solution of hoai, and repeat this operation frequently. After drying the cloth so treated, each time by exposure to sunlight, the late Mr. Walter Crum obtained, by following this method, only a faint green.

Blue Colouring Substances.

We have already cursorily noticed some blue and bluish-violet colouring matters of vegetable origin. Such blue substances, however, are practically of little use: the only immediate blue vegetable principle which deserves our attention is indigotin, a nitrogenous perfectly well chemically-defined principle, the produce of several plants, and probably also generated under certain conditions in the animal organism.

We shall first speak of indigotin as a chemical substance, without taking into account its variable origin. We shall next describe the natural history of the plants wherein indigotin is formed, and the industrial preparation of indigo,

its qualities and applications.

Indigotin has not been hitherto artificially produced with certainty, and the relations it bears to one or other of the great series of organic chemistry are only imperfectly ascertained: the elementary ultimate composition of indigotin is perfectly well known, and its formula, C_8H_5NO , or any multiple thereof, is thoroughly controlled by a great number of derivatives.

Indigotin may be obtained in a crystalline state by sublimation, and in that case the crystals exhibit a soppery reflection. If reduced to powder it is deep

^{*} Forclos, "Répertoire de Chimie Appliquée," v., 331, 1863.

blue, and the form of the crystals is a right rhomboidal prism, terminating in two strongly inclined planes.

Amorphous indigotin, as obtained by the oxidation of solutions of white indigo in contact with air, is deep blue, with a purplish hue, and assumes by rubbing a coppery lustre.

Indigotin volatilises at 290°, but the volatilisation is usually accompanied by partial decomposition; and only when the pure material is operated upon, and the volatilisation aided by some inert gas, decomposition is prevented.

Sublimed indigotin may, according to Dumas, be readily obtained by placing a thin layer of indigo in a clean frying-pan, and using another frying-pan as cover, the lower pan containing the indigo being cautiously heated, preferably on a sand-bath. Indigotin and indigo produce, when strewed over red-hot coals, violet vapours, not unlike those arising from heated iodine, and simultaneously a peculiar aromatic odour is given off.

Indigotin is insoluble in water, alcohol, ether, fatty and essential oils, and dilute acids and alkalies, either hot or cold. Creosote (Reichenbach's) and phenic acid and aniline dissolve a small quantity of indigotin at a boiling heat, but, on cooling, it is re-deposited. When finely pulverised indigotin is mixed with anhydrous acetic acid, and a single drop of concentrated sulphuric acid is added, there is obtained a beautiful deep blue liquid, from which the indigotin is separated unaltered on the addition of water. If the original acetic acid solution is applied to any woven tissue, and immediately afterwards washed in water, the tissue is dyed blue. It should be observed that this process is the only manner hitherto known in which indigotin, without being reduced, is reproduced in its primitive state. Indigotin is a thoroughly neutral substance, void of taste and smell; its sp. gr. is 1:35. When decomposed by dry distillation indigotin yields, among other products, aniline. By oxidising agents, such as concentrated solution of chromic acid and chlorine, indigotin is converted, when water is simultaneously present, into a new substance, which differs from indigotin only by having one atom of oxygen more in its composition, and which is named isatin. It is usually obtained from indigotin by the action of moderately diluted nitric acid. Strong and hot nitric acid converts indigotin into indigotic or nitrosalycilic and picric acids: in either of these reactions some carbon is eliminated, in the shape of carbonic or oxalic acid. The most interesting, and practically most valuable, property of indigotin is its great power of fixing hydrogen, and becoming converted into a colourless body, soluble in alkalies or alkaline earths, and capable of reproducing indigotin by simple exposure to the oxidising action of the air. This phenomenon of hydrogenisation, improperly called reduction, requires the hydrogen to be in the nascent state, and it is generally considered that this reaction can only take place in the presence of alkalies or alkaline earths only, but Schlumberger has observed this phenomenon taking place in an acid liquid, the conversion of indigotin into white indigo being quite complete.

It is well known that the freshly-prepared solution of zinc in sulphurous acid decolourises energetically the solution of sulphate of indigo, as well as other colouring matters. When a concentrated solution of sulphurous acid is poured over granulated zinc, the liquid becomes first yellow, and rapidly acquires this decolourising property, there being formed a mixture of sulphite and hyposulphite of zinc; none of the substances present in this mixture

possess, by themselves alone, the property of decolourising sulphate of indigo, and, moreover, this zinc solution only retains that property for a few hours. M. Schænbein* states that sulphurous acid and neutral sulphites barely act upon the solution of indigo in sulphuric acid, but that acid sulphites (bisulphites) decolourise this solution very energetically; the original blue colour is restored by the action of strong acids, alkalies, water in excess, lowering as well as raising the temperature, and other influences. The zinc solution also decolourises powdered indigotin if, simultaneously, ebullition be applied. The instance is the only exception to the rule that the reduction† of indigotin requires, and is effected by, the intervention of alkalies or alkaline earths, the latter acting as solvents for every particle of hydrogenised or white indigo. The resulting solution is a clear, transparent, golden-yellow liquid, which in contact with air becomes covered with a coppery-looking thin film of regenerated (re-oxidised) indigotin.

Dyers apply the term indigo-vats to solutions of reduced indigo prepared on

the large scale, by means which we shall presently explain.

The following substances have the power of converting indigotin (including of course indigo as well) into what is termed white or hydrogenised indigo. The substances and methods applied in practice on the large scale will be afterwards fully explained.

I. Alkaline metals: as might be expected, these bodies—which, in contact with water, yield hydrogen as well as an alkaline solution—are highly reducing agents, and their mode of action is greatly regularised by being made into amalgam with mercury. If sodium amalgam is brought into contact with finely pulverised indigotin and water, reduction rapidly ensues.

2. The metals and non-metallic elements which decompose water in the presence of an alkaline base, viz., tin, antimony, aluminium, phosphorus: these, bodies, however, only act when an alkali is present, and

require a higher temperature.

3. Such metallic oxides as are readily capable of higher degrees of oxidation, as, for instance, the protoxides of iron and tin.

4. The acids which, as phosphorous and hypophosphorous, are readily peroxidised; but these acids only act as reducing agents when bases are

nrecent

 Some sulphurets, phosphurets, and arseniurets; for instance, sulphuret of arsenic (realgar).

Such organic matters as are oxidisable in the presence of alkalics, as, for instance, glucose and gallic acid.

7. Reducing and alkaline fermentation, butyric fermentation.

Sulphur and the oxides thereof, of a higher degree than sulphuric acid, not only do not act as reducing agents upon indigotin, but are without any action whatever, even in the presence of alkalies, and it appears, even, that—as regards all the polysulphurets of the latter—they abstract from already-reduced white indigo its combined hydrogen, and precipitate, consequently, blue indigotin.

* "Poggendorff's Annalen," civ., 300.

[†] Although, as already stated above, this word is not precisely a correct expression for the real process hereby alluded to, we preserve its use here, since it is a generally accepted term.

The sulphurets which act as reducing agents—as, for instance, realgar, orpiment, the protosulphurets of tin and antimony—exert their reducing action as a consequence of their tendency to become oxidised by the influence of alkalies; the sulpharsenic and sulphantimonic acids, and bisulphide of tin, are inert.

On the small scale, the hydrate of protoxide of iron and glucose are frequently applied in chemical laboratories for the purpose of preparing indigovats. For this purpose the following mixture answers very well:-- I part of finely ground indigo,* 2 parts of pure sulphate of protoxide of iron, 3 parts of slaked lime in fine powder, and 200 parts of water: the dry substances are, when ground, well mixed together, and introduced into a narrow-necked flask, into which should be inserted a tightly-fitting cork; the water (best tepid) is poured in after the dry substances have been put into the vessel, which should be completely filled by the liquid, and immediately afterwards closed by the cork. The flask is shaken now and then, and left standing for several hours; the yellow liquid is a solution of white indigo in lime-water; the deeper yellow precipitate is a mixture of sulphate of lime and hydrated peroxide of iron. The reactions which take place in this experiment may be briefly summarised thus :- A portion of the hydrate of lime decomposes the sulphate of iron, forming hydrated protoxide of iron, which begins to decompose water, immediately the nascent hydrogen reacts upon the indigotin, converting it into white indigo, which in its turn combines with another portion of the lime, and becomes dissolved in water as a calcic compound-

 $\underbrace{2(C_8H_5NO)}_{\text{Indigotin.}} + H_2 = \underbrace{C_{16}H_{12}N_2O_2}_{\text{White indigo.}}.$

According to Fritzsche the glucose-vat is prepared as follows:—125 grms. of finely-powdered indigo, along with an equal weight of grape-sugar, are placed in a flask of about 6 kilos. capacity, filled partly with boiling alcohol at 71 per cent; to this fluid are added 200 grms. of a concentrated alcoholic solution of caustic soda, and next the flask is entirely filled with boiling alcohol; the flask, well corked, is shaken for a time, and then left standing; the clear supernatant liquid, having been decanted, yields, when stirred up in contact with air, a precipitate of blue indigotin, in the shape of copperylooking, small, needle-shaped crystals, these being only obtainable in the humid way by the process here described.

While it is easy enough to prepare white indigo in alkaline solutions, it is difficult to obtain that body in a pure and solid state,—a preparation which requires great care and dexterous manipulation. White indigo is so readily oxidisable, when once exposed to air, that the manipulations required for precipitating, washing, filtering, and drying it, cause it to be almost entirely re-converted into blue indigotin, unless it is completely kept from contact with air.

M. Dumas gives the following description of his process devised for preparing white indigo:—An indigo-vat, with sulphate of iron as above described, is made with 500 grms. of indigo, in a thoroughly-closed vessel suitable for the purpose: after having been left standing the clear liquid is, by means of a

^{*} Although somewhat difficult to pulverise, on account of a peculiar toughness of this substance, it is preferable not to purchase it in the powdered state, as it is then far more likely to be adulterated.

syphon, transferred to bottles previously filled with carbonic acid gas, and on the bottom of which is poured also some pure hydrochloric acid freed from air, in sufficient quantity to saturate the lime and precipitate the white indigo. Every bottle should be completely filled, stoppered immediately, and next immersed in a tub filled with water, and left standing until all the white indigo is precipitated. As soon as this is the case the clear supernatant liquid is withdrawn by means of a syphon, and the precipitate placed on a filter and left to drain under a bell-jar filled with carbonic acid gas: the precipitate is washed with cold water, freed from air by long-continued boiling, and cooled in well-stoppered bottles; the precipitate is next dried over sulphuric acid under the receiver of a good air-pump. White indigo so prepared is a coherent whitish-grey mass, of silky lustre, void of taste and smell, insoluble in water, soluble in alcohol, ether, alkaline solutions, and lime and baryta waters, forming yellow solutions. When in contact with air the white indigo becomes gradually blue, through and through; but this change takes place far less slowly than when the compound is moist. Oxidising substances produce the same effect, and this also applies to a comparatively slight elevation of temperature, which has the effect of turning the white substance suddenly blue: dry distillation decomposes this body, there being formed a small quantity of sublimed indigotin, while a bulky charcoal is left. Strong sulphuric acid dissolves white indigo, producing a deep purple liquid; after addition of water a solution of sulphindigotic acid remains.

White indigo is a very weak acid; it dissolves in and combines with alkalies, alkaline carbonates, and the alkaline earths; but the combination is so feeble that even the attraction of textile goods is sufficiently powerful to break it up,

and cause the precipitation of the acid on the fibre.

Many of the metallic salts yield, with the alkaline solutions of indigo, heavy, white, sometimes even crystalline, precipitates, which may be considered as constituting compounds of white indigo with the corresponding metallic oxides. Such are the following:—Salts of magnesia, alumina, zinc, protoxide of iron, cobalt, manganese, lead, silver, protoxide of tin. Salts of copper act as energetic oxidising substances, converting the white indigo into blue indigotin.

According to Berzelius white indigo forms two compounds with lime, a soluble and an insoluble, the latter containing excess of lime: this fact is of practical interest, inasmuch as if—in the making up the so-called copperas-vat—too much lime is added, a portion of the indigo will precipitate and remain

inactive at the bottom of the vat.

A boiling, concentrated, caustic potassa-lye, sp. gr. 1'45, containing about 45 per cent of dry caustic potassa, dissolves indigo, yielding an orange solution. On the addition of water the liquid becomes at first brownish-yellow, and deposits, when in contact with air, indigotin, while isatate of potassa (isatin + hydrate of potassa) remains in solution. There takes place, in this instance, an oxidation as well as a reduction of indigotin, according to the following formula:—

 $_3C_8H_5NO + KHO + H_2O = C_8H_6NKO_3 + C_{16}H_{12}N_2O_2.$

Isatate of potassa. White indigo.

The oxidation of this last body gives rise to the formation of indigotin: indigotin fused with caustic potassa gives off hydrogen, and is converted into

anthranilic acid $(C_7H_7NO_2)$, and if heated to 300°, along with solid caustic potassa, indigotin yields salicylic acid $(C_7H_6O_3)$, and when submitted to dry distillation along with caustic potassa, aniline (C_6H_7N) is formed.

Without entering here into lengthy details which belong strictly to the domain of theoretical organic chemistry, we may observe that these reactions evidently denote an intimate relation between indigotin and the phenyl group; salicylic acid, indeed, may be formed by the combination of carbonic acid with phenate of soda, whereby salicylate of soda is obtained, while anthranilic acid can be considered as phenyl-carbamic acid, and aniline as representing phenylamin. Dry indigotin is not acted upon by either chlorine or bromine, but if water is simultaneously present oxidation takes place, and isatin is first formed, but entering into combination with the haloids the ultimate result is the formation of substitution products, such as chlorisatin and bromisatin. Iodine has no action upon indigotin, either in the dry or moist state. Concentrated sulphuric acid yields, with indigotin, sulphoconjugated acids and sulphuric acid derivatives, the production of which depends upon the nature of the acid (fuming or ordinary), the duration of the contact, and the temperature applied. There are thus formed either sulphopurpuric acid (C₁₆H₁₀N₂O₂,SO₃) or sulphindigotic acid (C₈H₅NO,SO₂), or the hyposulphindigotic acid, which is described only by Berzelius, and the composition of which is not accurately known. Sulphopurpuric acid, also known as sulphophenicic acid, phenicin, and indigo-purple, is the product of the first moments of the action of sulphuric acid upon indigotin, and even when the contact of the acid and the indigotin is very short, especially if fuming acid be employed, it is very difficult to obtain sulphopurpuric acid perfectly free from sulphindigotic acid.

M. Camille Keechlin* states, contrary to the observations of Berzelius and Gerhardt, that when fuming acid is employed, though the contact of the acid and indigotin be only for a few minutes before the addition of water, no sulphopurpuric acid at all is obtained. He advises the use of strong common sulphuric acid. This last-named acid converts indigotin readily into sulphopurpuric acid; the best mode of preparing the latter consisting in mixing finely ground indigo with the acid, so as to form a homogeneous mass, which is to be poured at once into at least from fifty to sixty times its bulk of cold water, in order to prevent gradual conversion into sulphindigotic acid. The former acid is sparingly soluble in an acidified liquid; it is therefore deposited from the large bulk of water in the shape of a red flocculent body, which is collected on a filter, and washed with water slightly acidified with hydrochloric acid. This washing, however, is not sufficient to obtain the acid in a pure state, for which purpose wool-yarn or worsted should be immersed in a bath of it, and next washed in a solution of carbonate of soda, whereby the sulphindigotic acid which might have been present is washed out, sulphopurpuric retained, and may be removed by washing in acidulated water. A better method of purifying sulphopurpuric acid is to apply the unequal solubility of the potassa or soda salts of the two conjugate acids; the sulphopurpurate being far less soluble, it is clear that after careful neutralisation of the acid mixture, previously diluted, however, to some extent with water, the effect of a prolonged washing will be the elimination of the blue, while the

[&]quot;Bulletins de la Société Industrielle de Mulhouse," vol. xxiv., p. 331.

purple remains, and may be employed to dye wool in an acidulated bath. The aqueous solutions of sulphopurpuric acid are blue, and yield when neutralised with either an alkaline carbonate or acetate a purple flocculent precipitate; the ensuing alkaline salts are red in the dry state and blue in aqueous solution. Their solubility in water is not very great, r part of the potassa salt requiring 100 parts of water; even very dilute solutions of sulphopurpuric acid are precipitated by the salts of lime, magnesia, alumina, iron, tin, and copper. Reducing agents, such as protochloride of tin, albumen, &c., bleach this acid, but its colour is restored by exposure to air. Concentrated sulphuric acid converts sulphopurpuric acid into sulphindigotic acid, which latter is in its turn re-converted into sulphopurpuric acid by digestion with indigo. By long-continued boiling with water the colour of sulphopurpuric acid is converted into a deep blue; hot alkaline lyes turn it green, but in the cold alkalies are without action upon it, though they cause sulphindigotic acid to become yellow.

Sulphindigotic acid, C8H5NO,SO3, is readily obtained by the action of sulphuric acid either upon indigotin or crude indigo. When ordinary concentrated sulphuric acid is employed the best proportion is from 15 to 20 parts of the acid to I of indigo; the reaction is rendered more complete by the aid of a temperature of 40° to 50°; when fuming sulphuric acid (so-called Nordhausen) is used the proportion of acid is from 6 to 8 parts; the blue liquid (which, if fuming acid is used, inclines more to a purple) is poured into from thirty to forty times its bulk of cold water; any sulphopurpuric acid present is thereby thrown down, and after having been removed by filtration, there is obtained a deep blue liquid, containing sulphindigotic, and a certain quantity of hyposulphindigotic, acid. These acids are separated from each other, according to Berzelius, by immersing white woollen worsted yarn in the liquid; the dye is attracted by the wool, which is next digested for some time with a weak solution of carbonate of ammonia, whereby the coloured acids are re-dissolved. This solution is evaporated to dryness at 50° on a water-bath, and the dry residue exhausted with alcohol at 83 per cent strength, which dissolves the hyposulphindigotate of ammonia; the insoluble residue is taken up with water, and precipitated with acetate of lead; the sulphindigotate of lead having been collected on a filter and washed, is suspended in water, and decomposed by a current of sulphuretted hydrogen gas. The sulphide of lead being removed by filtration, the filtrate is at first colourless, but becomes blue by contact with air. On being evaporated at 50° sulphindigotic acid remains behind as an amorphous deep blue, hygroscopic mass, which has an acid and simultaneously astringent taste, and a pleasant very characteristic smell; this acid is very soluble in water and alcohol. The salts of this acid are blue, amorphous, and exhibit in the dry state very strongly the coppery lustre of good indigo. These salts are prepared either by the direct reaction of the acid and a base, or by the reaction of the acid with a carbonate or acetate, while the sulphindigotates, which are insoluble, or only very slightly soluble, may, of course, be prepared by double decomposition. The alkaline salts of this acid are very sparingly soluble in liquids which contain neutral salts in solution, as, for instance, chlorides of potassium and sodium, sulphate of soda, and, consequently, the alkaline sulphindigotate is precipitated as a flocculent matter when to any of its aqueous solutions a solution of any neutral salt is

added. Sulphindigotate of potassa requires 140 parts of water for solution; the soda salt is somewhat more soluble; the baryta salt is rather sparingly soluble in cold, but more readily so in hot, water; the lime, magnesia, and alumina salt are very soluble, but the lead salt is insoluble.

All reducing agents, such as mixtures of zinc and sulphuric acid, tin-salt, hydriodic and hydrosulphuric acids (at 50°), zinc and sulphurous acid, decolourise sulphindigotic acid. The alkaline salts, which are reducing agents, e.g., sulphites, also readily bleach solutions of sulphindigotates, but the blue colour is restored by the action of the air. Hyposulphindigotic acid may be obtained from the alcoholic solution of the ammoniacal salt by precipitating with acetate of lead, and decomposition of the lead salt by sulphuretted hydrogen. This acid is only distinguished by the solubility of its alkaline salts in alcohol at 83 per cent; practically this acid is of no importance.

The following is a brief summary of the results of the investigations made by Berzelius and Gros-Renaud on the sulpho acids of indigo when acted upon by alkalies and alkaline earths. These researches are indeed interesting, and might, if resumed and more fully gone into, produce useful practical results, since the savans just named found that these blue substances are capable of yielding red, yellow, green, and violet derivatives, which dye wool and silk without the aid of mordants. Hydrosulphindigotate of baryta in solution becomes green when evaporated on a water-bath; the residue, very soluble in water and alcohol, yields with subacetate of lead a greyish green precipitate, from which, after treatment with sulphuretted hydrogen, is obtained sulphoviridic acid, the solution of which appears green by reflected and red by

transparent light.

When sulphindigotate of potassa is mixed with 30 parts of lime-water, and this mixture submitted to heat in a sealed tube, a purplish liquid is formed; when, after opening of the tube, the excess of lime is precipitated by means of carbonic acid, and the liquid, after having been filtered to remove carbonate of lime, evaporated to dryness, the residue first washed with alcohol, and next treated with water, there is obtained a beautiful purple liquor, which yields, when precipitated with acetate of lead, a reddish-brown deposit, which, after having been treated with sulphuretted hydrogen while suspended in water, and after separation of the sulphuret of lead, leaves a purple liquid, from which, after evaporation to dryness, is obtained an amorphous brown mass, sulphopurpuric acid. When sulphindigotate of potassa is acted upon by lime-water in contact with air, the liquid becomes first red, next yellow. When the lime is withdrawn from the liquid while still red by means of carbonic acid, and the carbonate of lime is first filtered off, and the liquid next evaporated, a brown residue is obtained, from which alcohol at 82 per cent dissolves out a yellow compound. This yellow fluid yields, when precipitated with acetate of lead, a yellow mass, which, on being decomposed by sulphuretted hydrogen, produces sulphide of lead, and sulphoflavic acid, a yellow crystalline substance, after evaporation of its solution. The residue from the treatment with alcohol just named dissolves in water, giving a red liquid, precipitable by basic acetate of lead; the resulting lead salt having again been treated by sulphuretted hydrogen, yields, to absolute alcohol, after evaporation, sulphofulvic acid, a reddish-yellow substance; while the residue after treatment with absolute alcohol consists of sulphorufic acid, a red matter. Both these acids are amorphous and soluble in water.

M. Gros-Renaud's researches* gave in many aspects analogous results. When indigo-carmine (that is to say, sulphindigotate of soda as met with in trade) is suspended in water, and there is added to that mixture a caustic soda lye, of sp. gr. 1'333, containing about 30 per cent of dry caustic soda, there is obtained a yellow liquid and a black precipitate, soluble in water, with a blue colour. If to the yellow liquid strong sulphuric acid is added a few hours after it (the liquid) has been prepared it becomes blue, this colouration being permanent; if the acid is only added after twenty-four hours the liquid becomes first green, next red, and at last violet. When the yellow-coloured liquid is strongly acidified forty-eight hours after having been prepared it becomes rapidly red after having passed through a variety of intermediate hues. This red liquid dyes, if previously incompletely saturated with carbonate of soda, unmordanted wool, imparting to it tints varying from rose to deep amaranth-red, according to the concentration of the liquid and the length of the immersion of the wool, as well as the temperature. The violetcoloured liquid just before mentioned dyes wool violet. This red substance differs essentially from sulphophenicic and sulphopurpuric acids, being far more soluble in water, and becoming immediately yellow on the addition of a small quantity of caustic soda, but being rendered violet again by the addition of as much sulphuric acid as is necessary to neutralise the alkali. Acetate of lead does not form with the red matter any precipitate. Wool which has been dyed amaranth with this red matter yields, when treated with strong sulphuric acid, a red liquid, while wool which has been dyed with sulphopurpuric acid yields, under the same conditions, a blue liquor. The production of red or amaranth dyes upon wool with sulphopurpuric acid requires, after dyeing, an alkaline bath, which is unnecessary for the red liquor just named.

When caustic soda is made to act for three days upon a mixture of sulphindigotic and sulphopurpuric acids, and the liquid next supersaturated with concentrated sulphuric acid, there results a red liquid and a yellowish brown precipitate. This latter having been collected on a filter, and more or less washed, dyes deeper or lighter yellow shades, according to the more or less complete washing of the precipitate. It has not been hitherto possible to reproduce indigotin from its sulphuric acid derivatives, though frequent attempts have been made.

When indigotin is heated up to 180° along with chloride of benzoyl the former body is converted, with evolution of hydrochloric acid, into a brown matter, which fuses at 108°. It is soluble in alcohol and ether, and consists

of a benzoic indigotin compound, C₈H₄(C₇H₅O)NO.†

Isatin is a coloured matter, but not a tinctorial product, about which, however, since it is an immediate derivative from indigotin, and, moreover, formed during some of the industrial applications of that body, viz., during the application of the discharge style upon blue-dyed grounds by means of oxidising substances, we give the following particulars:—Isatin is produced by the action of oxidising agents upon indigotin, such as chlorine water, dilute nitric acid, chromic acid, ferricyanide of potassium, and caustic alkalies. It is best prepared by mixing I kilo. of finely pulverised indigo with water, so as to form a thickish paste, to which, while being gently heated, there are

^{* &}quot;Bulletins de la Sociéte Industrielle de Mulhouse," vol. xxiv., p. 343.

t "Comptes Rendus de l'Académie des Sciences," lvi., p. 1050.

gradually added from 600 to 700 grms. of common nitric acid. As soon as the blue colour has disappeared a large quantity of water is added, the liquid next boiled, and filtered while still hot. From the filtrate impure isatin separates in the shape of a brown amorphous mass, which being accompanied by a rather large quantity of a semi-fluid resinous matter, is, in order to eliminate that substance, dissolved in caustic soda, and next very carefully neutralised by hydrochloric acid, and immediately after filtered. By this process the resin is separated, and in order to obtain isatin from the deep orange filtrate it is only requisite to acidulate the liquor thoroughly, whereby the isatin is separated as a crystalline deep orange-red body, sparingly soluble in cold, but better in hot, water; soluble in alcohol, ether, benzin, and consisting of C₈H₅NO₂, that is is say, indigotin plus oxygen. Isatin is converted by nascent hydrogen at the ordinary temperature into isatyd, a white, very sparingly soluble substance, which bears the same relation to isatin as white indigo does to indigotin. When isatin and isatyd are heated together to 130° in sealed tubes, along with either hydriodic acid or with biniodide of phosphorus and water, they are converted into a mixture of insoluble products, viz., isatopurpurin, a red substance, soluble in alcohol and ether; isatoflavin, a yellow matter, insoluble in ether, but soluble in alcohol; and, lastly, a deep green substance, insoluble in alcohol and ether. These bodies are derivatives from isatin by the elimination of oxygen, and may be viewed as polymers of indigotin, with more or less oxygen in their composition. The reproduction of indigotin from isatin by this reaction has not been successful, not a trace even of that substance being found.

Caustic potassa converts isatin into isatic acid, while chlorine forms chlorisatin and bichlorisatin, and bromine mono and bibromisatin. Isatin combines with ammonia, forming, while water is simultaneously eliminated, imesatin, imasatin, isamic acid, isamid, and isatimid. Sulphurous acid combines with isatin, provided either potassa or ammonia be simultaneously present, yielding compounds known as isatosulphites. Isatyd combines with sulphuretted hydrogen to form sulphisatyd and bisulphisatyd, the sulphur taking the place of a portion of the oxygen of the compound.

According to M. Laurent, the action of caustic potassa upon isatyd produces a red body, indin, which, although not fully identical with isatopurpurin, is very similar to it. An alcoholic solution of caustic potassa converts indin and the sulphatisyds into hydrindin, a white or light yellow body, and into flavindin, a deep yellow substance. Dr. Schützenberger has obtained similar

products by the reducing action of hydriodic acid upon isatin.

The substance known as indigo is chiefly a product of vegetable origin, but occurring also or formed in the lower as well as higher organised animals, including man, in some rare pathological cases of production of a blue urine and blue pus. Indigo has undoubtedly been known in Asia from a very remote period of antiquity, since there exist in very ancient records, written in the Sanskrit language, descriptions of its mode of preparation, mainly not different from the methods yet in use. The ancient Greeks and Romans have also been acquainted with this drug, as proved by the testimony of Pliny, while the ancient Egyptians dyed linen and cotton fabrics with indigo, since pieces of woven tissues dyed blue with this substance have been occasionally found among the wrappings of mummies.

During the middle ages indigo had become almost unknown in Europe, but it is quite certain that now and then some small quantities came to Italy by way of Alexandria, and it was used there to some extent. The old Dutch East India Company (1602) first brought indigo from India via the Cape to Europe in large quantity. The introduction of this dye-ware into Europe gave rise at various times to legal ordinances and acts of Parliament in England prohibiting its use. It was called a "devilish drug," pernicious to the growers of woad (Isatis tinctoria), and injurious to the fabrics; but, notwithstanding severe opposition, as early as 1631 half a million pounds of indigo were brought in one year to Amsterdam and sold at very high price. Shortly after the discovery of America it was found that some parts of that country also produced plants from which indigo could be obtained.

The plants which yield indigo are rather numerous, and do not all belong to the same family, though none of them contain the colouring matter ready formed. It owes its origin to a peculiar colourless principle, about which more hereafter, and which is converted into indigotin by a process of fermentation.

Among the indigotin-producing plants the most important are the genus Indigofera, belonging to the natural order of the Leguminoseæ. The following are the names of the more important plants cultivated for its production:— Indigofera tinctoria, Indigofera disperma, Indigofera anil, Indigofera argentea. The following are less frequently planted, or, at any rate, less valuable:— Indigofera pseudotinctoria, hirsuta, sericea, cytisoides, trifoliata.

These plants are natives of Guzerat, but have been cultivated from time immemorial in the rest of Hindostan, especially Bengal, Java, the Philippine Islands, and also in China, though there to a far more limited extent. The Spaniards brought some of these plants over and acclimatised them in several parts of their former extensive South American possessions. The roots of the Indigoferas are very fully developed, and the plant exhales, especially towards night time, a strong and somewhat disagreeable odour. The taste of the leaves is disagreeable, and they putrefy rapidly when immersed in water. The experience of the indigo planters in Java is that the natives who work in the factories and handle the plant in various ways are liable to suffer from sexual impotence, accompanied by a temporary semi-lameness of the lower limbs. The exhalations emanating from indigo fields where the plants are grown produce headache and nausea to those not accustomed to the smell. Indigo is used internally as a therapeutic agent of some repute against cataleptic and other fits.

The indigo plants are grown in India from seed sown in a loamy soil, previously thoroughly well ploughed and dressed. The sowing seasons are in the spring and autumn, according to the special kind of the plant, the nature of the soil, the situation of the field in reference to water supply, because on low lying lands subject to inundations the crops must be gathered before the rivers are swollen by rain. As soon as the young plants are sufficiently forward they are re-planted in regular parallel rows, care being taken to weed out from the soil any useless parasitic plants. The flower buds are pulled off before they are fully developed, experience having taught that by so doing the leaves of the shrub become larger and yield more indigo, the colourable matter which produces that substance being chiefly present in the leaves. In some localities the leaves, which have become bluish green, are pulled from

the plant and gathered, but in most cases the entire plant is cut down close to the ground about the months of June or July, when the few flower buds left begin to open. The roots left in the soil soon sprout again, producing a second and even in some instances a third and fourth crop of the shrub, but in each case the quality of the product becomes weaker both in quantity and quality. The plants when cut down are collected in bundles and brought to the factory before evening, so that they may be operated upon at once.

M. Kæchlin-Schwartz* has published an interesting account of the manufacture of indigo as carried on in Lower Bengal. The following is an abstract of that paper:—Lower Bengal is renowned for the excellent quality of its indigo, and the factories are among the best which exist as regard all arrangements, containing filters, presses, cauldrons, and boilers; drying rooms, large water tanks, and, lastly, the very essential tanks for the extraction of the leaves by means of water. These tanks are placed in two rows, containing from 15 to 20 each, one row being placed higher than the other. The tanks are built firmly of brickwork, lined inside with a strong cement; their shape is rectangular, about 6 metres by 6.5, and from 0.9 to 1.0 metre in depth; the uppermost row of tanks is placed about 0.9 metre higher than the lower range. The tanks of the upper range serve for the purpose of the fermentation of the plant.

Pure water in large and almost unlimited quantity is an absolute requisite of an indigo factory, and in this respect the situation on or near the Ganges is of great importance; the water of that river is relatively very pure, and in order to cause the deposition of suspended matter it is brought by conduits into large ponds, and, after having become clarified, is conducted to large tanks, which are on the same level with the masonry tanks just described. The plant being cut down in the forenoon is delivered in neatly made-up bundles at the factory in the afternoon. The bundles are placed neatly in the tanks, each containing 100 thereof, and care is taken to pack them tightly. while they are prevented from floating by the placing of stout pieces of timber across the tank tightly wedged. It is essential that there should be left as little open space as possible to ensure the proper progress of the fermentation. As soon as the tanks are filled with bundles a sluice valve is opened, which causes the water to run in, and so to fill them that the bundles are entirely submerged. The process of fermentation goes on more or less slowly, according to the prevailing temperature, but it lasts on an average from nine to fourteen hours. The progress of the operation is considered good when a small quantity of the liquid from the fermenting tanks, run off into the tanks of the lower row, exhibits a straw colour; for although the quantity of the product will in that case be rather less abundant, the quality will be better than if the colour of the liquor be golden-yellow, and a turbidity be apparent at the same time. When the liquor is run off from the fermenting tanks its colour is more or less yellow; after having been left at rest for a few moments twelve naked men descend into the tanks and begin to stir the water very vigorously, while at the same time the fermenting tanks are emptied, cleaned, and made ready for another operation. The operation of stirring and beating the water is continued for several hours, there being seventeen workpeople, viz., twelve men and five women, employed to each tank. While this operation is going

^{* &}quot;Bulletin de la Société Industrielle de Mulhouse," vol. xxviii., p. 307.

on the colour of the liquor becomes gradually pale green, and the indigo becomes visible, being in a state of suspension as a flocculent matter. As soon as this change is complete the workpeople leave the tanks, and, after the liquid has been left at rest for a time, the supernatant water is run off gradually by the opening of plugs placed from the top to near the bottom of the tanks at convenient distances apart. The water flows again into the river, and the precipitated indigo, in the form of a thickish semi-fluid mass, runs along a spout into a well-constructed tank. This mass is next drawn up by the aid of a hand-pump, and conveyed to a large cauldron, where it is boiled with the view of preventing a further fermentation, which would spoil the produce by turning it black. After having been left at rest for twenty hours in the cauldron, of which, in a large factory, there are at least five often heated by means of steam, the pasty mass is boiled again for from three to four hours, and next, while yet hot, run on to a large filter, constructed in the following manner:-In a large tank of masonry of 6 by 2 metres and 0.9 metre deep, are placed pieces of bamboo cane, over which are spread lightly woven mats, and next over these a strong piece of sail-cloth. Upon this latter remains a thick deep blue, nearly black, paste; the water collected in the tank still deposits some indigo, and is therefore boiled up again the next day, and afterwards filtered. The pasty and still very soft mass which remains upon the sail-cloth is removed to small wooden boxes, perforated with holes, and lined inside with a stout and strong cotton tissue. These boxes having been filled, and a lid having been put on the top, likewise perforated, and so constructed as to fit in, not on, the boxes, care being also taken to place a piece of cotton on the top, the boxes are placed under a screw-press, and pressure having been gently and gradually applied, the water is squeezed out as much as possible, that liquid being run again to the filter tank to collect any indigo it may yet contain. The pressure having been withdrawn the boxes are opened, and the contents, shaped like blocks of soap, are placed in the drying room; this is a large and high brick building, containing a series of windowlike openings, closed by Venetian blinds, so as to prevent the access of direct sunlight; while, moreover, there are planted outside and close to the building large trees for the same purpose. The process ought to proceed very slowly; and it takes from three to five days to dry the contents of each box. Artificial heat is not required, but in case of heavy rain shutters are put up outside the Venetian blinds. As soon as the cakes of indigo are thoroughly dry they are packed in well-made wooden boxes, the seams of which are made water-tight with pitch, and are often lined with sheet zinc or tinned sheet iron. After having been packed the drug is sent to Calcutta, the chief market. Each fermenting tank produces from 18 to 25 kilos. of indigo if the plant be grown on alluvial soil, and from 16 to 32 kilos. if cultivated on older formations. The quality of the former produce is, however, preferable to that of the latter. The spent plant (after fermentation) is only used as manure. The plants shoot out again if properly placed in the soil, but the indigo they would produce would be altogether of a low quality, and not pay the expense and trouble of the manufacture.

The details above quoted refer to the manufacture of indigo as carried on by European planters, provided with a sufficiently large capital to defray the heavy expenses of establishing works and beginning cultivation. The natives carry on operations in a somewhat similar manner, but working on a small scale, do not succeed so well, and the quality of their produce is inferior. The average quantity of indigo annually made in the Bengal Presidency amounts to about 4 millions of kilos.

M. Twist* states that in the Guzerata country the leaves of the indigo shrubs are dried in the sun, and next steeped for four or five days in pure water, previously poured into well-made tanks, care being taken to stir the mixture occasionally. The liquid is run off from the tanks after lapse of the above time; and, after having deposited the indigo as a semi-fluid mass, the supernatant clear liquid is slowly run off; and the indigo having been thrown on to a coarsely-made but thick and tightly-woven woollen cloth, is left to drain, and next dried in the sun. The natives of the above-named country are in the habit of adding to the yet pasty mass some blue mineral, or clay.

The Chinese cut the plants in the manner above described, and treat them further in the same way as already mentioned; but they add powdered slaked lime to the mass in the fermenting tanks, thereby causing a more rapid deposition of the precipitate afterwards. The Chinese also dry the indigo in the sun, according to some authors.† It is rather doubtful whether the statement concerning the drying of indigo exposed to sunlight is quite correct.

M. Keechlin-Schwartz relates what he has seen during a journey and lengthy sojourn in Bengal; and he was told that the exclusion of sunlight is absolutely necessary to ensure good produce; yet a great many authors, among them those named in the foot-note below, speak of drying in the sun, which, as regards Twist, is a communication made from personal inspection on the spot. From private communication made to us by a Java indigo planter we can reconcile these discordant statements; the fact is, that as long as the indigo is still soft and pasty, so that it can easily receive impressions from the finger, it is kept in the shade, and almost in the dark, being merely exposed to strong ventilation; but as soon as the mass has become dry and sufficiently solid to bear handling, it is further dried during the daytime in open air, being placed upon hurdles made of bamboo, and purposely exposed to the sun, provided there be no danger of rain. This proceeding is also carried on in Bengal, but is very frequently there done not at the factory, but at or near Calcutta, and has therefore been overlooked by M. Kæchlin-Schwartz, who has also forgotten to mention the care taken with regard to the boxes, as above specified, in which the indigo is sent over to Europe. The fact is, that the ware is packed for sea transport, chiefly at Calcutta, being sent thither from the factories, when fit for handling though not quite dry, in light bamboo baskets, as kindly communicated to us by Mr. J. A. Longridge, C.E., who has travelled in India while on Government duty as Inspector and Reporter on Railways. The process of indigo manufacture in America and the West Indies is similar to that already described. In southern China, and especially in Kouang-si, Kouang-toung, and Fo-kien, indigo is largely produced for home consumption only.

We have now to consider the theory of this process of manufacture. The following questions arise: —What are the chemical phenomena observed during

^{* &}quot; Descriptio Guzeratæ;" a very rare book.

[†] Sloane, Gaertner, Lamarck, Plagne ("Annales Maritimes," 1825). Vilmorin, "Journal d'Agriculture Pratique," i., 449. Hervy, "Journal de Pharmacie," xxvi., 290.

the process of the fermentation of the plant, and under what influence and from what substance present in the plant is indigo derived? Since no researches on the fresh indigo plants have yet been made, and since, moreover, the different phases of the operations whereby indigo is produced on the large scale have never been scientifically examined, we can therefore only reason by analogy or from observation of what happens with other similar plants, and give an explanation which is probably, but not necessarily, correct. It has been at one time supposed that the leaves of the Indigoferæ contained indigotin in the hydrogenised state, and that this substance became soluble under the influence of a peculiar fermentation, while the stirring and beating of the fermented liquid afterwards by promoting contact of the liquid with air caused the oxidation of the white indigo. Although this explanation agrees with the well-known chemical properties of indigo, it is not tenable on account of the following facts:-The yellow liquid which runs off from the fermentation tanks has a decidedly acid reaction (according to Dr. Croockewit, who, by a lengthy residence in Java, has been frequently enabled to test this liquid), and contains both acetic and lactic acids; and we know by experience that white indigo is not soluble in an acid liquid, and only dissolved by the aid of alkalies or alkaline earths; and unless we therefore admit the existence of an unknown principle, capable of keeping white indigo dissolved in such a liquid as that running off from the fermentation tanks until it is oxidised by the oxygen of the air, the existence of the hydrogenised indigotin in the plant is not very probable. Another opinion is, that indigo does not pre-exist in the leaves or plant at all, but is formed during the process of fermentation which is usually employed for the extraction of the drug (dye material) from the indigofera as well as from woad.

Dr. Schunck has discovered in the *Isatis tinctoria*,* a principle very soluble in water and alcohol, viz., a kind of glucoside, capable of being split up by the action of dilute acids and alkalies, and even simply by evaporation of its solutions into a peculiar sugar (indiglucin) and into indigotin; to this product the chemist just named gives the name of indican, its formula being C₂₆H₃₇NO₁₇: the splitting-up of indican into indigotin and indiglucin may be elucidated by—

 $\underbrace{C_{26}H_{31}NO_{17} + 2H_2O = \underbrace{C_8H_5NO}_{Indigotin.} + 3\underbrace{(C_6H_{10}O_6)}_{Indiglucin.}}_{Indiglucin.}$

The preparation of the indican will be referred to when we treat of woad; but it is probable indican may exist also in the Indigofera; and, if so, the indican will become soluble in the fermentation tanks, and this body in solution will be entirely split up into indigotin and indiglucin in the beating tanks, a result which, under the prevailing high temperature (often 30° to 35° C.), will cause the further decomposition of the indiglucin, and also cause the production of other brown, red, and yellow matters, which remain mixed up with the indigo. During the process of beating up the liquor a large quantity of carbonic acid is disengaged, and consequently a good ventilation has to be kept up in the buildings wherein the tanks are placed. If the temperature of the liquid is too low (the workpeople know by experience the most suitable temperature) hot water is added, but is rarely needed.

Indigo is only, or at least chiefly, prepared from the real Indigofera, although

^{*} This dyeing material, known as woad, will be more fully mentioned below.

the following plants, which are used for blue dyeing, contain likewise indigotin, viz., the woad, or pastel, Isatis tinctoria; Polygonum tinctorium, largely cultivated in Russia, and there applied for the manufacture of indigo; Nerium tinctorium, Asclepias tingens, Eupatorium tinctorium, Galega tinctoria.

According to Dr. Schunck, indigo-blue is obtained from the leaves of Blesia Tankervillia, a fact established also by the late Dr. Calvert. They contain also indican, which the former chemist considers to be in every case the parent substance of indigotin. Dr. Schunck did not succeed in obtaining indigo-blue from the Galega tinctoria and Spilanthes tinctorius grown in the open air in this country, but considers it possible that the colour might be developed in a warmer climate.

Woad, or Pastel (Isatis tinctoria), is a biennial plant, belonging to the Crucifera. Its leaves are gathered in the month of June of the second year, and are sometimes simply cleaned, and serve, after having been dried, for the purpose of dyeing; more frequently, however, the leaves are converted by the aid of water into a paste, which is heaped together to a height of from 90 centimetres to 1 metre, and left fermenting for about a fortnight, and then made up into the shape of small balls, similar in size to those sold as washing blue. In some few instances the fermented mass is submitted to another fermentation, which is accompanied by a disengagement of ammonia. The material thus obtained is known in the trade (at least on the Continent, since woad and its preparations are quite out of use in England)* as pastel; the best kind thereof is made in Provence and Languedoc; next in value is the Normandy; while the growths of Thuringia, Bohemia, and Hungary are of equal quality. Pastel is very frequently used for dyeing along with indigo, and some dyers pretend that they cannot get good shades without it. Pastel balls of good quality should be light, exhale a sweetish odour, have a green or greenish yellow colour, and should when cut exhibit a greasy lustre, and leave when rubbed on paper a greenish streak. They improve in tinctorial power by being kept, so that when six or eight years old their value is nearly doubled. It does not appear that indigo ever has been industrially prepared either from pastel or the fresh plant, but there is no doubt that it can be obtained from these substances; and before the re-introduction of indigo in Europe in the 17th century woad was generally applied for dyeing a fast blue.

From the dried leaves of the same plant Dr. Schunck obtained indican by the following process:—The leaves are treated with cold alcohol; to the liquid thus obtained water is first added, and it is next concentrated by evaporation at the ordinary temperature, aided by a current of dry air. The concentrated liquid is filtered and shaken up with freshly precipitated hydrated oxide of copper. The liquid is again filtered, and the filtrate treated with sulphuretted hydrogen to eliminate the oxide of copper which had been dissolved. It is again filtered, and the filtrate evaporated by the aid of a current of air at the ordinary temperature until there remains a syrupy mass, from which indican is extracted by cold alcohol. This solution deposits a brown material, and on the addition of ether other foreign matters are thrown down. The liquid having been filtered is evaporated, leaving indican as a light brown, syrupy, bitter mass, which has an acid reaction with test-paper; it is soluble in water, alcohol, and ether, and susceptible of yielding, under the influence of acids or of a ferment in the plant, indigo-blue and sugar.

^{*} Woad, though no longer used as a dye, aids the fermentation of the indigo-vats.

To obtain this interesting decomposition with acids, it is simply necessary to heat the indican with strong sulphuric or hydrochloric acid, when the indigo precipitates, while the sugar remains in solution. But indican is so liable to undergo modification that, if the action of the acids be continued, besides the indigo-blue an indigo-purple is formed, called by Dr. Schunck Indirubin. This author's researches have a very important bearing upon the manufacture of indigo, since they show that under the influence of a ferment the indican is converted into sugar and white indigo; and they also explain that if the manufacturer is not very careful he may experience great loss in the amount of indigo obtained. Dr. Schunck has observed that indican, when dissolved in water, is liable to undergo rapid modifications, and that instead of yielding, in contact with acids, indigo-blue and indirubin, it gives indiretin, indihumin, and other compounds of decomposition.

Indican is met with as an ordinary constituent of human urine and blood, and also the blood of oxen. Its discovery in blood is due, we believe, to Carter. The plant botanically known as the Isatis indigotica, in China Tein-hoa, Tein-ching, is a native of that country, and is largely cultivated for the purpose of manufacturing a kind of indigo, which is sold in a pasty, viscous state, since when once dry it only yields a blackish tint on dyeing. It is used as a fast blue dye at Canton, Emoui, and other places. The Polygonum tinctorium, a herbaceous plant of the natural order of the Polygoneæ, is also used in China for the purpose of indigo manufacture, yielding a material of good quality; but according to M. Natalis Rondot, the plant, called lau in Chinese language, is not the Polygonum above mentioned, but a kind of asclepiad. However this may be, the Polygonum tinctorium has been acclimatised in Europe from seed obtained from China. The small quantity of indigo it yields, only about 1 per cent on an average, was not found to make the cultivation a paying business* in those parts of Europe where indigo is readily obtainable.

M. E. Schwartz states that the indigo obtained from the *Polygonum* is not so good as that obtained from India, in so far as the colouring value of the former is less. The yield also of the plant varies according to its age, the climate, the nature of the soil, &c. The manufacture of indigo from the *Polygonum* is performed precisely in the same manner as is above described for the preparation of indigo.

The indigo obtained by the process above described from the different species of the Indigoferæ may vary considerably as regards its richness in tinctorial matter, and the quality also of the latter differs sometimes considerably. This is due to various causes, among which are the following:—In the first place, too frequently, sufficient care is not taken in carrying out the manufacturing process, the workmen, and even the planters, being often entirely ignorant of the principles upon which the manufacture is based. There are also employed different varieties of plants, gathered under atmospheric conditions, which are not the same year by year; while, moreover, the ripeness of the plants and the nature of the soil on which they are grown are of considerable importance.

The following kinds of indigo are distinguished in commerce, according to

^{* &}quot;Bulletin de la Société Industrielle," vol. xi., p. 186; xii., 216; xiv., 212. "Journal de Pharmacie," No. 5, May, 1840.

the countries whence they are imported:—Asiatic indigos, from Bengal, Oude, Madras, Java, and Manilla. African, imported from Egypt, Mauritius, Senegal. American, from Guatemala, Caraccas, Mexico, Brazil, the Antilles, and South Carolina.

The Bengal, Java, and Guatemala indigos are considered the best; these varieties exhibit the following general characteristics:- Java indigo contains generally the colouring matter in a very pure state, along with a minimum of extractive organic matter; but in some of the sorts of this drug the quantity of indigotin is greatly decreased by the amount of siliceous matter present. This indigo feels soft, and adheres strongly to the tongue if pressed against it. The sp. gr. of this material is low; its colour a pure soft blue, the inferior qualities exhibiting an ash-grey hue, while the superior qualities are magnificently violet-blue, and assume, when rubbed with the nail, a beautiful coppery hue. The Java indigos, although not the very richest in indigotin, are superior to all others as regards the purity and beauty of the colouring matter; they, moreover, contain no carbonate of lime, and are, also on account of the very small quantity of organic matter they contain, in very high request for the manufacture of indigo carmine. Practical dyers complain that Java indigos do not work well, their tinctorial value, i.e. the amount of wool they will dve up to a given shade, being smaller than their appearance, either in the lump or in solution, would lead the observer to expect.

The Java indigo is imported chiefly, but not exclusively, into Holland, and is packed in very carefully-made wooden boxes, weighing when full from 20 to

60 kilos.; the ware is in square or cubical cakes.

Bengal indigo is the indigo par excellence, on account of the yield, including a great variety of sorts from the richest to the most common. This ware comes chiefly to London in the shape of large prismatic lumps, packed in wooden boxes, containing from 130 to 140 kilos. The higher qualities are a deep blue violet. The paste is very homogeneous and fine grained; it adheres to the tongue, but less strongly than Java indigo. Bengal indigo is easily pulverised, and exhibits also, when rubbed with the nail, a coppery hue; it contains on an average about 72 per cent of indigotin. The sp. gr. of indigo is on an average, according to M. Ziurek, =0.769, while that of indigotin is = 1.35. The brokers distinguish no fewer than forty-five different kinds of Bengal indigo, among which are certain varieties which exhibit a reddish hue, due to the presence of a larger quantity of a brown extractive matter, which, indeed, far from acting injuriously on the dyeing operations, seem to exercise a beneficial effect, because it appears to assist the fixing of the indigo on the tissues. Dyers very generally prefer the reddish Bengal indigo, but reject the light blue kind, which has a strong greyish or greenish tint, and is hard and dense, containing a large amount of an inert extractive matter. Such indigo scarcely adheres to the tongue, and does not, on being rubbed with the nail, assume a coppery hue. There is met with among the Bengal qualities a variety which is light blue, yet rather free from extractive vegetable matter, but contains a large quantity of mineral impurities, and for the rest exhibits pretty much the characters of the last-named sort.

The Oude and Coromandel Indigos are generally heavy, brick-shaped masses, difficult to break, approaching in tinctorial value the medium fine Bengal kinds, and are further distinguished into violet and ordinary copperylooking.

Manilla Indigo is found in light, brick-shaped, or irregular masses; colour light blue; fine-grained and homogeneous; it effervesces with acids, in consequence of containing carbonate of lime. This indigo is rarely used for dyeing, being too poor, but it is largely employed for making washing-blues. It also is imported in wooden boxes, generally weighing from 50 to 60 kilos.

Madras Indigo: fine blue or bluish-violet, less rich than, but equally light (specifically) as, Bengal indigo, and characterised by the feature that the cakes have retained the impression of the folds and texture of the cloth on which it was placed while soft. The low Madras qualities have an unpleasant greenish hue, and contain sometimes 50 per cent of mineral matter. The boxes in which it is sent to Europe weigh on an average from 80 to 90 kilos.

Guatemala Indigo occurs in small irregularly-sized lumps, packed in serons—bags or bales made of cow-hides, weighing about half as much as the Bengal boxes. The Guatemala indigo is, as regards quality and variety, not unlike the Bengal, but the ware is never so well sorted, and therefore generally less valuable: the light blue kind is more rare amongst this indigo, and when it occurs it is poorer in colouring matter than the same variety of Bengal indigo. The reddish-coloured Guatemala is not well suited for dyeing, since it is very poor in blue, and contains too great an excess of brown extractive matter. Notwithstanding these defects the indigo in question often contains excellent qualities. The distinguishing marks or brands are—Indigo Guatemala flor, Sobre saliente, and Corte.

Caraccas Indigo resembles greatly the last-named kind, but is generally less esteemed: it is packed in surons.

Mexican Indigo stands between the two last-named, but does not of late years come into the market any large quantity.

From a paper published* by M. R. E. Meyer on a sample of indigo manufactured in Cochin China, we learn the following particulars, first, as regards that sample, and secondly, about some other varieties of indigo:-The Cochin China growth consists of small, flattened, irregular lumps, weighing from 3 to 6 grms. each. Judging by the impression left on the surface, the paste has been pressed between linen while yet wet: the colour is a pure bright blue, without any violet hue. It adheres to the tongue, exhibits a coppery gloss, is very homogeneous, and its fracture does not show any foreign substance. The author estimated the indigotin in this ware, and found its average quantity to be 51.85 per cent, while the estimation of this colouring matter in the following sorts of indigo gave the following quantities: -Bengal, ordinary deep blue, heavy substance, not adhering to the tongue, 55: Bengal, deep reddish-blue, 63.5; Bengal, fine violet-blue, light (specifically), 68.25; Bengal, superior quality, 69.5; Guatemala, very common brownish-blue, 55.25; Guatemala, bright blue, common sort, 57.75. The author was unable to obtain either any of the Java or of the best Guatemala kinds. The quantity of ash present in the Cochin China indigo amounts to 22.36 per cent, consisting chiefly of phosphate of lime, accompanied by small quantities of carbonate of lime, iron, alumina, magnesia, soda, but not even a trace of potassa; traces, however, of copper and lead were found, due to the vessels employed in the manufacture. The ash in Bengal indigo only amounts to 6.63, and in two varieties of Guatemala to 11.34 and 7.28 per cent.

^{* &}quot;Bulletin de la Société Industrielle de Mulhouse," May, 1870, p. 253.

Brazil Indigo occurs in small rectangular blocks, or irregular lumps: it is firm, breaks readily, the fracture is not conchoidal; it assumes, also, when rubbed with the nail, a coppery hue, and is externally greenish-grey.

Carolina Indigo is in the shape of small lozenges, externally grey: both the last-named sorts are superior in quality to the other American products.

Among the improvements Egypt owes to its last three rulers, the cultivation of indigo-producing plants is not one of the smallest: the result is, that for about the last twenty-five years there has been in the market an excellent quality of this ware, met with in the shape of flattened cakes, of fine-grained texture, very light, and coloured either pure blue or pure violet-blue: it is packed in boxes.

Senegal and Mauritius Indigos are rarely seen in the market, but are, generally speaking, of very good quality.

Low qualities of indigo are characterised by a dirty, more or less greenish, colour, a coarse and unequal texture, and great specific gravity; they do not adhere to the tongue, and do not become coppery by friction with the nail. Such are never of any real use to the dyer, notwithstanding the low price at which they are offered. The fact that some samples of indigo contain only from 12 to 14 per cent of indigotin is of itself sufficient proof of the necessity of adopting scientific investigation for the proper valuation of this ware. Such indications are of immensely more value than the empirically obtained, often useless, valuation and sorting of the brokers. All indigos which contain a large percentage of impurities are a loss to the dyer, since these cause by their presence a loss of colouring matter, which is rendered unavailable and inactive.

The best kinds of indigo for use in the so-called cold-vat, for dyeing linen and cotton,* are the medium good qualities of Bengal and Guatemala, and especially the reddish varieties: the inferior qualities just mentioned are less injurious when applied in the so-called hot-vats, used for dyeing wool; and this branch of industry consumes the inferior kinds to a large extent. For the purpose of calico-printing the better qualities only of indigo are used.

The following are a few of the trade terms applied to indigo generally, without reference to the country of its production:—

Sandy Indigo, containing much earthy matter.

Ribboned Indigo, exhibiting various shades of colour, running in the shape of ribbons.

Spotted Indigo, the colour varying from spot to spot.

Burnt Indigo, when it happens that the ware, on pressure in the hand, falls to black pieces.

Large Squared Indigo, when the cakes are broken up into several large lumps.

Half Broken Indigo, when the cakes are broken in two only.

Coarse Granulated Indigo, the ware broken into comparatively small lumps.

Cold Indigo, when the ware does not adhere to the tongue.

Fig Indigo, a very low quality, used possibly by the makers of laundry blues. Since indigo is an expensive dye-material, and since its value depends not only on the percentage of indigotin it contains, but also on its physical

^{*} Cotton yarn, we need hardly state, is dyed blue in the hot copperas bath.

properties, hardness, specific gravity, the quantity and nature of the foreign matters it contains, either naturally present or fraudulently added, all these conditions have to be studied when a sample of indigo has to be reported on, and the chemical assay of the ware is preceded by a physical examination, for which purpose several pieces are taken and attentively examined. First, as regards the recent fracture, it should be seen whether the different cakes contained in a box are alike, and whether the fragments broken off from one and the same lump exhibit the same hue. The porosity of the sample is examined simply by applying the moist tongue to the recently fractured lump; the greater the adherence to the tongue the greater also will be the porosity of the indigo. The coppery lustre of the drug is determined by rubbing it with the nail, and the specific gravity is taken by the well-known method of weighing with the 1000-grain bottle. By these determinations, aided by practice, some idea of the value of the ware may be obtained, and a great many dyers do not apply any other tests at all; but even the most experienced men are liable to errors, and it is therefore better that the quantity of indigotin should be estimated, but this estimation, however valuable in a sense, is also not sufficient by itself. When the percentage of indigotin in two samples is the same, the preference should be given to products which are light and soft, and for the application to indigo-vats it is best to take the violet-red in preference to the bright blue kinds.

For the quantitative estimation of indigotin many methods have been proposed, but some of these are not sufficiently accurate, while others are too cumbrous and lengthy, and hence not available when a large number of samples have to be analysed simultaneously. We shall here only quote the really useful methods, and those which are actually applied or capable of being so. A weighed quantity of indigo is dried at 100°, and next exhausted by boiling water, weak acids and alkalies, and alcohol (indigo is soluble to some extent in the latter liquid when boiling and very concentrated, but is redeposited on cooling); the residue left after these operations, deducting from the weight thus obtained the quantity of ash as determined by the ignition of a separately weighed sample, is considered to be pure indigotin. The presumption is that this body is insoluble in all the liquids applied, while the foreign matters are withdrawn.

M. Pungh proposes the following method, which, although accurate, takes too much time, and is hence impracticable where several samples have to be assayed:—30 grms. of previously dried indigo are mixed with lime and sulphate of iron (see "White Indigo"); the clear liquid is decanted, and the sediment submitted to another reduction process. The joint liquids are oxidised and precipitated by an acid; the indigotin which is thrown down is collected on counterpoised filters, washed, dried, and weighed. A certain weight of woven tissue or yarn may be also dyed by this process, and the quality of the indigo judged from the intensity of the colour.

M. Mittenzwei* reduces the indigo by means of an alkali and a proto-salt of iron, pours on the liquid a layer of light petroleum oil, takes—by means of a curved pipette—a known volume of the clear liquid, and introduces this into a graduated tube containing a known measured bulk of oxygen gas standing in a mercurial trough: from the quantity of gas absorbed the quantity of indigotin

^{* &}quot;Journal für Praktische Chemie," cxi., 81 .

is calculated, it being known that r grm. of this material absorbs 45 c.c. of oxygen gas while being converted from white into blue indigotin. This method is utterly unfit for the commercial laboratory, and still more for the workshop, warehouse, or dye-works.

Another series of methods are based upon solution in sulphuric acid: for this purpose, however, only the strongest fuming acid, sp. gr. 1.89 to 1.92, is available; but what is then quantitatively determined is not so much indigotin as the sulphindigotic acid, and this portion of the process varies in different methods. Sometimes the assay is a colorimetrical estimation, the liquid, of course, having been diluted to a certain invariable bulk; or a weighed quantity of wool is dyed with the sulphindigotic acid.

Another group of methods for the quantitative estimation of indigotin previously converted into sulphindigotic acid depends upon the use of an oxidising material which can be used in the shape of a titrated liquid; for instance, solution of chlorine, of bleaching-powder (hypochlorite of lime), of bichromate and permanganate of potassa, &c. The end of the operation is readily enough seen, since it coincides with the total destruction of the blue colour of the substance. If the normal liquid can be preserved without undergoing any change, it is only required to determine exactly the quantity of indigotin converted into sulphindigotic acid which can be decolourised by I c.c. of the oxidising liquid; but it is undoubtedly better as advised by M. H. Schlumberger, that whenever an assay is made, the experimenter should operate upon equal quantities of pure indigotin and of the sample to be valued at the same time.

Berthollet first suggested the use of chlorine: this method has been improved upon by M. H. Schlumberger, and is executed as follows:-Weigh off exactly I grm. of each of the samples of indigo to be tested, and previously dried at 100°, and very finely pulverised; weigh off also 1 grm. of pure indigotin (easily obtainable, in dye and calico-printing works, from the vats, and to be washed previous to use, first with acidulated water and next with pure water); the substance is put in small porcelain capsules, and thoroughly mixed with 12 grms. of strongest fuming sulphuric acid; the capsules are covered with glass plates, and kept standing for at least twenty-four hours at a temperature of from 20° to 22°; the liquid is diluted with water so as to fill a litre measure: take of that fluid 59 c.c. by means of a graduated pipette, pour it into a suitable glass vessel, and add next, gradually, by means of a burette, a weak solution of hypochlorite of lime, at a strength of 1° Baumé (sp. gr. 1.007), in quantities of about 2.5 c.c. at a time; cease adding as soon as the blue colour is entirely destroyed: in order to estimate the excess of chlorine which may have been used, there is added, drop by drop, from a burette, a solution of sulphindigotic acid: the same solution, as above mentioned, may do, until a yellow-greenish hue reappears. Suppose that 5 c.c. of the bleaching-powder solution have sufficed to decolourise exactly 50 c.c. of sulphate of indigo (viz., 50 c.c. primitively taken, and 9 c.c. added to restore the greenish-yellow colour). It is, however, advisable not to rely upon one experiment, but to repeat it to judge more correctly. Suppose, further, that 46 c.c. of the indigotin taken-treated, of course, as has been mentioned for the indigo-is also equal to 5 c.c. of the chlorine solution, then the following simple proportion will serve to calculate the results:-46 c.c. of sulphuric

indigotin = 59 c.c. of sulphuric indigo; 59 c.c. contain therefore 0.046 grm. of indigotin; how much is contained in 1000 c.c.? or how many times x is contained in I grm. of $x = \frac{4.6}{5.0} =$ the weight of indigotin contained in I grm. of indigo. This process is deficient in the following particulars:-The solution of bleaching-powder changes, and therefore has to be tested afresh, and its value in relation to indigotin estimated whenever a new series of experiments is commenced—say at one or two days interval; it is also impossible to guard completely against loss of chlorine at the moment of mixing the hypochlorite solution with the acid indigo or indigotin solution. In consequence of these defects this process has been improved upon by substituting for the use of chlorine other more manageable oxidating matters, as, for instance, permanganate of potassa, by itself; a mixture of chlorate of potassa and hydrochloric acid; and bichromate of potassa mixed with the last-named acid, as proposed and carried out by the late Dr. Penny. This method has met with general approbation, especially at the hands of the Mulhouse and other Alsatian manufacturers, who unanimously speak in favour of this process, based upon the following facts: - When very finely pulverised indigo is acted upon by very strong fuming sulphuric acid, the foreign organic matters it contains are carbonised, and remain behind upon the filter, after the addition of water, while the indigotin becomes soluble; when to this solution first hydrochloric acid is added, and next to the previously thoroughly warmed fluid bichromate of potassa, the sulphindigotic acid is decomposed and converted into sulphisatic acid. When, therefore, a titrated solution of bichromate of potassa is employed, it is plain that the amount of indigotin may be calculated from the volume of the bichromate solution used to destroy the blue colour.

It has been found, by experience, that in order to bleach a given weight of indigotin, in the shape of sulphindigotic acid, the quantity of bichromate required is precisely that which is necessary to convert the indigotin into sulphisatic acid: the reaction is very precise, and as long as any indigotin remains the bichromate only attacks it: 3 molecules or 393 parts of indigotin require 1 molecule or 297'2 parts of bichromate, or, percentically, 100 parts of indigotin require 75.6 parts of bichromate. This process is executed in the following manner: - The sulphuric acid solution of indigo is made with 1 grm. of that substance, and further proceeded with as above stated in Schlumberger's method; the titrated bichromate solution is to contain 7.66 grms. of the pure salt to the litre: I c.c. of this liquid corresponds to 10 c.c. of a solution of I grm. of pure indigotin to the litre, equal to o'or grm. of indigotin, so that every c.c. of this fluid is equal to I centigrm. of indigotin. Take 100 c.c. of the diluted solution of indigo in sulphuric acid, boil it gently in a porcelain basin, add to c.c. of hydrochloric acid, and add next with the burette the bichromate solution, taking care to cease adding the very moment the greenish hue disappears and makes place for the orange-yellow colour. M. Meyer, in the paper above quoted, while testing by this method the various kinds of indigo, found that the end of the operation is not so readily seen as is generally stated, because the colour of the sulphisatic acid is rather more a deep vellowish-brown than orange-yellow; the original colour of the indigo solution being deep blue, the disappearance of that colouration is, according to him, somewhat obscured from view. It is, at all events, always desirable to make two, if not three, estimations of the same sample: the number of tenths of cubic centimetres of the chromic solution consumed gives directly the

percentage of indigotin contained in the indigo under examination. In order to obtain reliable results by this method it is, in the first place, necessary to take a fair average sample of the indigo, by breaking off lumps from a number of the cakes or squares contained in a chest; the next point to be attended to is the pulverising of this substance so as to be really an impalpable powder, to be sifted through a very fine silk-gauze sieve, every morsel passing through the sieve. After the indigo has been acted upon by the fuming sulphuric acid, and this fluid has been diluted with water, that solution must be carefully filtered, in order thereby to remove the brown-coloured particles of extractive matter which float about, and which, by their presence, might give rise to errors of more than 15 per cent in the estimation of the indigotin, especially for the lower sorts of indigo. When the indigo is dissolved in the fuming sulphuric acid, it may happen that sulphurous acid is given off; * this is sometimes present in the fuming acid itself, but it is completely removed before water is added: if, however, the indigo happens to contain iron in the state of peroxide, that body would, by the action of the sulphurous acid, be reduced to protoxide, and would of course in that case vitiate the action of the bichromate by taking up some of that for its own oxidation. In case, therefore, indigo contains peroxide of iron, it is necessary to treat it, previous to estimating the indigotin, with boiling dilute hydrochloric acid-a precaution also required when the indigo contains a large amount of carbonate or other salt of lime.

Indigo as met with in commerce rarely, if ever, contains so much iron as to make the use of hydrochloric acid necessary, but it sometimes happens that in dye-works indigo residues from the vats have to be analysed which contain a large proportion of iron, and in that case the treatment with hydrochloric acid becomes necessary.

Some chemists propose to dissolve the indigo in flasks, aiding the admixture of the ware with the acid by the addition of some few grains of lead shot; but by adopting this method the escape of the sulphurous acid gas is prevented, and it is preferable to conduct the operation in porcelain capsules or basins.

M. H. Schlumberger has published† a comparative review, in tabulated form, of the value of different kinds of indigo: the highest proportion of indigotin was found by him in a superfine purplish-coloured Java indigo, at 96 per cent, a figure which M. E. Schlumberger considers by far too high: the researches on this subject of Dr. G. J. Mulder, who has been for nearly forty years the analytical chemist and scientific referee to the Dutch Society of Trade and the Dutch Indian Department, prove that occasionally a few samples of indigo, some few boxes, have been sent from Java containing indigo of great purity, but the average varies from 16 to 82 per cent for different qualities, and the superior is a rare article, not daily met with. M. E. Schlumberger states that by using the bichromate process, and testing by it various kinds of indigo, he found that the quantity of indigotin averaged from 12 to 72 per cent.

^{*} The production of sulphurous acid by the action of the sulphuric acid upon the impurities of the indigo is a very grave objection to the use of all decolourising methods. The errors thus produced are considerable, and become greater the lower the quality of the sample. Dr. Schunck—certainly no mean authority—considers that no rapid and trustworthy means of determining the amount of indigo-blue in commercial samples is known.

^{† &}quot;Bulletin de la Société Industrielle de Mulhouse," xv., 277.

The impurities which are found in indigo along with indigotin are either natural or have been artificially added. Among the first-named we find—

- 1. Water of hydration, which varies on an average in quantity from 3 to 6 per cent, and is readily estimated by drying at 100°.
- 2. Various saline matters; among them phosphates and carbonates of lime and magnesia, sulphate and chloride of potassium; also silica, oxide of iron, in variable quantity: the lime salts are, however, the principal constituents of the ash, and are present in quantities varying from 3 to 7, and even 20, per cent. The quantitative determination of the ash of indigo is best executed by the careful incineration of about 5 grms. of the sample placed in a platinum crucible: the residue, after ignition, may—of course after having been weighed—be analysed or tested qualitatively, as suits the operator's object,
- 3. Indigo contains some brown and red organic matters, insoluble in water, but soluble in other liquids, among which are boiling acetic acid, boiling alcohol, ether, and caustic alkalies: these organic substances more or less modify the dyeing operation executed in the vat, and affect the blue colour imparted to a greater or less extent: if, for instance, the red colouring matter predominates, that substance becomes reduced, in the same manner as indigotin, by the action of the alkali, and in the dyeing process becomes precipitated upon the fabric along with the last-named principle, and causes thereby a purplish colour different from that produced by pure indigotin: even if this latter substance is prepared in the crystalline state by the glucose vat process, and therefore apparently quite pure, it yet frequently yields, when treated with boiling acetic acid, a certain quantity of red matter, which appears to belong to the same class of bodies as isatopurpurin, one of the products of the reduction of isatin by hydriodic acid.

We may here mention that indigo-blue has been artificially prepared by Emmerling and Engler ("Berichte der Chemischen Gesellschaft zu Berlin," No. 17, 1870), and that it has been obtained by Dr. Schunck by the action of strong acids upon normal healthy urine.

According to Berzelius, indigo contains gluten, soluble in dilute acids. The substances which are added to indigo for the purpose of adulteration are rather numerous, and vary in kind with the more or less refined knowledge of the persons who commit this fraud, either wilfully or from sheer ignorance, being induced to believe that some foreign substances promote the action of fermentation and precipitation of the indigo while being prepared as above described. Among the adulterants are starch, resins, logwood and its extract, Prussian blue, earths artificially blue-coloured, and it is said sometimes, though rarely, German ultramarine: the detection of these bodies offers no difficulty when the operator bears in mind what are the natural constituents of indigo, as above laid down: -Starch is converted into sugar by boiling with a dilute acid; resin is soluble in alcohol; logwood dissolves in water, giving rise to a solution which turns red on the addition of oxalic acid, and yields a blue precipitate with aluminate of soda; Prussian blue gives, on being treated with an alkaline solution, ferrocyanide of potassium; mineral substances can be recognised after incineration, and if any ultramarine is present this will be readily detected by becoming decomposed by dilute mineral acids, with escape of sulphuretted hydrogen.

Industrially-Prepared Sulphuric Acid Derivatives of Indigo; Indigo Carmine; Purple-Blue, also known as Boiley Blue.

For the purposes of dyeing and printing woollen and silk fabrics and yarns, and likewise for the purpose of imparting a blue hue to white cottons, indigo is frequently dissolved in sulphuric acid, whereby blue soluble compounds are obtained which exhibit a shade different from that of indigo, and are more readily applicable in dyeing. About thirty or forty years ago the solution of indigo in sulphuric acid was only known and used after having been properly diluted with water, being technically designated Saxon blue, or "chemic." It is clear, however, that this liquid, besides being very acid, contains also the brown and resinous matters present in native indigo. The preparation, moreover, of this solution was subject to variation, since in almost every dye-works the respective proportions of acid and indigo differed, while some manufacturers used ordinary strong sulphuric acid only, others again fuming acid, and some a mixture of both; it accordingly depended entirely on the doses of acid and indigo, the duration of contact, and the temperature, whether sulphindigotic, sulphophenicic acid, or a mixture of the two, was obtained; and since the shade produced by these acids is not the same, it is clear that, according to the tint preferred by the different makers, the choice of the prescription for making the dye-material differed also.

M. Persoz* advises the following receipt for preparing the above solution:-I kilo, each of finely ground indigo and fuming and of ordinary, but strong. sulphuric acid; leave the mixture standing for forty-eight hours, and next heat on a water-bath until a drop of the fluid, taken out by means of a glass rod, dissolves in water without producing a precipitate; after the mixture has cooled, it is diluted with water so as to form a fluid of 1.134 sp. gr.; 18° Baumé. M. Haussmann used 6.5 parts of fuming sulphuric acid for 1 part

of indigo.

Another mode of preparation is to add gradually, and by small quantities at a time, I part of pulverised indigo to 5 or 6 parts of very concentrated fuming acid, or from 10 to 12 parts of ordinary concentrated sulphuric acid: this mixture is left standing for twenty-four to forty-eight hours, and is next poured into twenty times its bulk of cold water, and filtered.

There is a very great difference, not to say discrepancy, between the different receipts for dissolving indigo, in respect of the proportion of indigo and acid prescribed to be used. According to Dr. G. J. Mulder, who investigated the cause of this difference, it is chiefly due to the fact that various kinds of indigo and the products of various countries do not behave alike in this respect; the superior sorts of the drug are less easily acted upon, and, as is also observed by M. Meyer, a really good and ready solution can only be obtained, in a comparatively short time, by the use of very strong fuming acid, and even then heat is required for the richer kinds: with inferior kinds the action of the acid is often weakened by the presence of lime compounds, but, if these are first removed by boiling with weak hydrochloric acid, the action of fuming sulphuric acid dissolves these inferior kinds rapidly, and with less expenditure.

M. Marnas recommends to withdraw colour from the dilute acid solution by means of woollen or worsted yarn. This fibre, having taken up the colouring

^{* &}quot;Impression des Tissus," vol. i., p. 454.

matter, is first washed with water, and next with a weak alkali, which redissolves the blue pigment, and the resulting solution is applied for dyeing purposes. At present, however, the dyeing of the so-called Saxon blue is effected by means of a preparation which has received a series of names; among them the following:-Indigo carmine, soluble indigo, cerulein, ceruleosulphate, precipitated indigo, extract of indigo. The manufacture of this preparation, which is in reality either a sulphindigotate or a sulphopurpurate of an alkali (chiefly, if not exclusively, soda), is based upon the almost absolute insolubility of alkaline sulphindigotates in any aqueous saline solution. In order to illustrate the mode of formation of the preparation in question, let us suppose that I part by weight of indigo is dissolved in from 4 to 6 parts by weight of the strongest fuming sulphuric acid, and that the resulting liquid is diluted with from sixty to eighty times its weight of water; this liquid will contain, beside sulphindigotic acid, an excess of sulphuric acid: when, therefore, there are gradually added to the liquid crystals of carbonate of soda, so as to neutralise all the acid (which requires in this instance from II to II'5 parts of the carbonate), there will be found not only sulphindigotate of soda, but also sulphate of soda, and by the presence of that salt the sulphindigotate of soda is precipitated as a deep blue flocculent matter. This material is collected on a filter, and more or less washed to remove the sulphate of soda, and sold as a paste, which, when dry, assumes a coppery hue, and this the more strongly so the richer it is in sulphophenicic acid. It often happens that these pastes contain an impurity, a dirty green matter, which can become fixed upon wool and silk. This impurity, which impairs the colour of the indigo carmine, may be detected by exhausting an acidulated aqueous solution of the carmine with wool, previously mordanted with alum and cream of tartar, because the green matter will be left in the solution. Another plan for detecting this impurity is to place a small heap of the indigo-carmine paste upon a sheet of white filtering-paper, when, after the lapse of some hours, the circumference of the heap will exhibit a green-coloured margin.

The preparation is commercially sold in different qualities, according to its richness in colouring matter. The simple extract contains, on an average, 4'96 per cent of indigo, 89 per cent of water, and 5'7 per cent of saline matter. Double extract contains, in 100 parts—Indigo, 10'2; water, 85; saline matter, 4'8. Triple extract—Indigo, 12'4; water, 73'7; salts, 13'9. While becoming dry the pasty carmine is covered with a saline efflorescence, which, according to M. Pohl, is prevented by mixing from 3 to 4 per cent of glycerine with the paste. The thoroughly dried, at least air dry, paste is commercially known as indigotin, and exhibits a blue colour: such a substance is prepared, according to Mr. Watson's method, by pouring the liquid resulting from the solution of 1 part of indigo with 6 parts of sulphuric acid upon 2 parts of chloride of sodium. The mixture is heated, by means of steam, until no more hydrochloric acid gas escapes; there is thus formed a dry residue suitable for dyeing and printing purposes; instead of common salt, caustic potassa, carbonate of soda, or also magnesia, may be applied.

The purple-blue of MM. E. and L. Boiley is a peculiar solid extract, prepared in the following manner:—From 10 to 20 parts of dry bisulphate of soda are fused in a cast-iron vessel, and when in full fusion there is added, by small quantities at a time, 1 part of indigo; the mass swells up and appears to boil;

INDIGO.

the application of heat is continued until a small quantity taken out and put in water dissolves completely, with a violet colour. The product of this reaction is then dissolved in from seventy to eighty times its weight of water, to which are next added 2 parts of common salt for every 1 part of the mixture of indigo and bisulphate; the precipitate thus produced is washed with water containing salt in solution, and next dried.

Indigo may also be converted into indigo carmine by mixing it with anhydrous sulphuric acid (the solid substance), dissolving the mixture in water, neutralising with carbonate of soda, and precipitating with chloride of sodium.

The Boiley blue is a crystalline, light purplish mass, yielding, when dissolved in water, a beautiful blue-violet solution: it is soluble in concentrated boiling acetic acid, depositing, on cooling, large prismatic coppery-hued crystals; it is insoluble in alcohol and ether; soluble in water, but more readily in hot than in cold: this solution is red when viewed by transmitted light. The substance in question is probably chiefly composed of sulphopurpurate of soda, and is remarkable on account of its ready crystallisation: its chemical properties, however, in many respects resemble those of the sulphuric acid compounds above named. It yields, with the chlorides of barium and strontium, violet precipitates.

The tinctorial value of indigo-carmine can be ascertained by a dyeing process, viz., a piece of woollen tissue is taken, and placed in an acidulated solution of the carmine to which cream of tartar has been added.

The following are the principal sulphuric preparations of indigo used at present in dyeing and printing:—

"Chemic," "chemic-blue," or "sour extract," is the solution of indigo in sulphuric acid, without any neutralisation or subsequent treatment. The following receipt may be used for its manufacture:—Take I lb. refined indigo, perfectly dry and in very fine powder, and stir it gradually into 15 lbs. of the strongest sulphuric acid. Let the mixture stand for three days, at a temperature of from 120° to 140° F. On dilution with water no sediment should appear. Some makers vary the quantity of acid, using only 12, 10, or 9 lbs. per lb. of indigo. Sometimes the acid solution is diluted with water to such an extent that it can be filtered through flannel, and is afterwards re-concentrated. If unrefined indigo is used the quality is inferior, as there is no means of getting rid of the brown and green colouring matters.

The paste, or "sweet" extract, varies very much in its degree of acidity. The following are formulæ for its preparation, beginning with the most acid:
—Stir I lb. of indigo, dry and in fine powder,—conditions which are imperative in all cases,—into 5 lbs. of sulphuric acid. The mixture is kept for ten to twelve hours at a temperature of 100° F. It is diluted with 4 gallons of hot water, filtered through flannel, and washed with hot water till the liquid runs through nearly colourless. The liquid is then concentrated to 3 gallons, 4 lbs. of common salt are added, and the mass thrown upon a filter to drain. The filter consists of a stout wooden frame, about 3 feet square, supported on a stand, either fixed or movable. No iron must be used in the construction of the frame. It is "dressed," as it is technically called, with a stout, compact, white woollen cloth. Over this is placed a layer of stout fine canvas, and

over this again fine calico. This triple filter is held in its place by ribs of wood pegged down to the frame.

Another mixture is—to lbs. indigo, stirred into 80 lbs. sulphuric acid, as before. Care is taken that the heat does not rise too high during mixing. Allow the whole to stand for twenty-four hours, at the temperature of 80° F.; then add 5 gallons of water, and mix well. Next dissolve 80 lbs. common salt in the smallest possible quantity of water, and add it to the indigo solution. The whole is then thrown upon the filter and allowed to drain.

The following receipt is given for a "sweet" extract of the first quality:—Take 4 lbs. of the best indigo, dry, well ground and sifted through a lawn or silk sieve. Add to it by degrees 37 lbs. of the best sulphuric acid, stirring well, and not allowing the heat to become too strong. Let the mixture stand at about 60° to 70° F. for eight days. Next dissolve 40 lbs. of clean common salt in water, and pour the solution into the acid. Then dissolve 60 lbs. of soda crystals in water, and add it gradually, lest the mixture should froth over. 2 lbs. of precipitated chalk are next added: the whole thoroughly stirred up, thrown upon the filter, and allowed to drain. The liquid that drains through the filter will be green: if its shade continues very deep, it is well to wash the paste on the filter with a weak solution of salt till the drainings become nearly colourless. The yield from the proportions given should be 120 lbs.

It will be observed that in this formula the indigo is not added to the acid, but the acid to the indigo, which, it is maintained, produces a richer and purer colour.

For a second quality, 8 lbs. of indigo are treated with 74 lbs. sulphuric acid, 144 lbs. of salt, 112 lbs. of soda crystals, and 4 lbs. of chalk, working in the same manner.

For a red extract of indigo, consisting chiefly of sulpho-purpuric acid, and resembling Boiley's purple-blue, take r lb. indigo, 3½ lbs. sulphuric acid, and leave them in contact, after incorporation for twenty minutes only. Then throw the solution into a very large excess of water, and wash with water containing a little hydrochloric acid.

Extract in which the acid is entirely neutralised is called "free extract," "soluble indigo," and frequently, though improperly, "indigo-carmine." They are in the form of a dry powder. Some good authorities maintain that carbonate of magnesia is preferable to soda for neutralising extracts.

All these acid preparations of indigo should be perfectly free from undissolved particles, which, if present, are very liable to render the goods spotty in the dyeing process.

The paste extracts should form a rather consistent mass, of a purple colour, without any green or brown reflection.

Extracts of indigo are sometimes adulterated with farina and other inert matters. This fraud may be detected by dyeing comparative swatches with the suspected sample against an extract of known purity.

The more acid varieties of extracts are applied on wool and worsted, whilst the more neutral are reserved for silk and cotton goods.

The material commercially known as refined indigo may be obtained by two different processes:—The one consists in treating common indigo, in fine powder, several times with strong hydrochloric acid not containing free

INDIGO. 467

chlorine: a gentle heat is applied, whereby not only the iron and lime and other mineral substances are dissolved, but the amylaceous matters present are converted into dextrin or sugar, which is removed by subsequent washing. The indigo is next treated with a weak solution of caustic soda, which dissolves the chlorophyll and other organic impurities. A still purer quality of indigotin (refined indigo of commerce) may be obtained by adding to a large quantity of water r part of finely-ground indigo, 2 parts of sulphate of protoxide of iron (green copperas), and a quantity of caustic soda slightly in excess of that necessary to neutralise the sulphuric acid of the copperas. The mixture is boiled and allowed to settle, when the supernatant liquor is run off from the sediment and well agitated, in order to convert the white soluble indigo into the blue insoluble form, which is collected and dried. The insoluble sediment is treated several times with a weak solution of caustic alkali, in order to remove the whole of the indigotin which it contains.

In order that indigo may be used for the purposes of dyeing, printing, and for the preparation of extracts, &c., the ware has always to be pulverised in the first place, and this pulverisation must be so effected as to produce an almost impalpable powder. If this is neglected, a loss of colouring matter is the result. Very frequently this dye ware is ground in a wet state, whereby the loss ensuing by the flying off of dust is prevented; but where the indigo is required for conversion into extract the addition of water is inadmissible. In almost all other cases the indigo is first steeped in water for some time, in order to soften it, as in its ordinary state it is a peculiarly tough, and even somewhat fibrous, substance. It is put in a suitable tub or trough, hot water is poured over it sufficient to cover it, and the tub is then closed with a lid and left standing for a day or two, until the water has been absorbed and penetrated into the entire mass; 10 kilos, of indigo require 15 litres of water.

In this country indigo is frequently pulverised on the large scale by drysalters, but in many cases dyers prefer to carry out this operation at their own works. Among the various simple apparatus in use for that purpose we mention briefly the following, which consists of a nearly hemispheric copper vessel, of 0.7 metre diameter, and furnished at its upper rim with two handles. The operator puts this vessel on a wooden bench, and seats himself thereon crosswise; he next puts three large cannon-balls, 12- to 18-pounders, into the vessel, and also a quantity of previously softened indigo and some water: by means of the handles a circular oscillatory motion is imparted to the vessel, and the balls, partaking that movement, reduce the indigo to the state of an impalpable pulp: after a certain time the liquid, containing finely divided indigo in a state of suspension, is poured into a tub, and a fresh quantity of water is added to the residue in the copper vessel; the agitation is resumed, and continued until all the dye ware is properly divided. On the large scale various machines are used for this purpose, the construction of which differs very greatly: some of these contrivances are arranged upon the same principle as the hand-mill just described. One of the best machines consists of an iron or copper cylinder, placed horizontally, and made to turn on a horizontal axis; inside of this cylinder are placed two rows of loose, movable, cast-iron cylinders, consisting of loose pieces, discs as it were, and set in the longer axis of the larger hollow cylinder. Since the tangential lines of the cast-iron cylinders and of the internal surface of the hollow cylinder differ,

being greater than that of the cast-iron cylinders, the result, on motion being imparted to the hollow cylinder, is that the inner cast-iron cylinders turn in a direction opposite to that of the large hollow cylinder, and the consequence is an enormous friction, which reduces the softened indigo to a pulp. This apparatus works very well if indigo of superior-or at least good ordinaryquality is to be operated upon, since these are readily and uniformly penetrated by water; but low qualities of indigo are often with difficulty, or even not at all, penetrated by water, and if brought into this apparatus the result is to convert the ware into a plastic, tough, semi-dry, clay-like mass, which soon causes the stoppage of the proper working of the apparatus. In order to guard against this contingency the previously softened ware is submitted to a preliminary grinding process, by means of a mechanical contrivance consisting of two circular cast-iron discs, placed horizontally and near to each other, but with a perceptible open space left between: by means of suitable machinery a rapid movement is imparted, one of the discs moving from right to left, the other from left to right; on the internal surfaces of the discs grooves are cut, somewhat like those on the stones used for grinding corn. The indigo is admitted to the spaces between the two discs, and is squeezed out at the circumference as a kind of thickish paste. This machinery may be applied for the pulverisation of other solid substances, and acts very satisfactorily.

Indigo can only be used for colouring textile fibres after having been previously rendered soluble, and this can, as yet, be effected only by the two methods already described,—the reduction process, and the action of concentrated sulphuric acid. In the first method the process of dyeing is based upon the regeneration of the indigotin, which then adheres to, and probably unites with, the fibre: by the second method the colouring matter has itself entered into a combination from which it cannot be again separated, so that the dyeing process is really carried on with a substance altogether distinct from the original indigo, and possessing other properties.

Fixing Indigotin by the Reduction Method.

The hydrogenisation of indigotin and the combination of white indigo with an alkali, or an alkaline earth, render it soluble, so that it can be made to penetrate textile fibres, and when the white indigo is, by suitable oxidising agents, re-converted into blue indigotin, that substance, becoming insoluble, is fixed in the pores of the textile fibres in such a manner as to adhere firmly and be capable of withstanding washing and soap. This reaction is employed for the purposes of dyeing in the following manner:—

1. The indigotin is reduced and dissolved by an alkali, and the fabric im-

mersed in the solution; ordinary indigo-vat.

2. The solution is printed or painted on some portions only of the fabric, by the aid of a pencil—so-called pencil-blue. Pencil-blue is supposed to be so called because originally used for the "enlummage" of madder chintz work, being pencilled into white spaces left for that purpose, such as leaves, &c. The pencil was simply a small, flat, blunt-pointed piece of wood.

The white indigo is precipitated in the form of a paste, in combination or
mixture with a very strongly reducing metallic oxide (commonly hydrated protoxide of tin), whereby the too rapid oxidation of the white

indigo is prevented. This paste, properly thickened, is printed on the fabric, which is next passed through an alkali-bath, lime water or soda solution, which has the effect of replacing the oxide of tin and forming a soluble combination of white indigo, which latter penetrates the fibre and becomes fixed by a subsequent oxidation process; so-called precipitate or fast blue.

4. Indigo, previously pulverised, is printed on the tissue, and this latter is next placed in such condition that the indigo may become dissolved and reduced locally, after which it is fixed by a subsequent oxidation; so-called China blue.

It is quite clear that for each of these methods any of the known processes of reduction may be used, care being, of course, taken to apply that which is practically the most advantageous.

The greatest consumption of indigo is for forming the blue vats in which woollen or cotton goods are dyed, by simply immersing them in the solution of white indigo. The same vat is not equally adapted for wool and calico, and, as will be seen in the following details, there is a wide difference in their composition.

Reduction of Indigo; Theory of the Indigo-Vats.

The most convenient method of reducing indigo for dyeing calico and cotton varn is based upon the action of hydrated protoxide of iron in the presence of lime, since it possesses, when recently precipitated, the property of reducing indigo, provided lime be simultaneously present. Any other caustic alkali would answer the purpose, but lime is preferable on account of its cheapness, and because it gives to the vats greater stability, the oxidation of the indigo being greatly lessened, owing to the formation of a thin film of carbonate of lime on the surface of the liquid, and, secondly, because with lime the chemical activity is less intense. The very rapid alteration of vats made up with caustic soda prohibits its use in dyeing yarn and tissues in the indigo-vat (vat-blue), and also prohibits the use of reducing agents, which are more advantageous than hydrated protoxide of iron, but do not act in the presence of lime. Lastly, but not least, we ought to observe that experience has taught that the lime compound of white indigo yields its colouring matter more readily and completely to the fibre than the corresponding soda compound, and, as a consequence, the vat is more completely exhausted, even when quite cold. The hydrated protoxide of iron is formed in the vat itself, by the action of the slaked lime upon the green copperas employed. This latter salt should not contain any sulphate of copper, because the oxide of that metal acts as a most energetic oxidising agent on the reduced indigo, which, therefore, would be precipitated in the vat itself. Basic sulphate of peroxide of iron and sulphate of alumina also ought not to be present in the copperas, because these substances would seize upon a portion of the lime and act as inert matter.

Copperas in solution is readily purified by boiling it with clean metallic iron, which precipitates any copper present in the state of metal, while any basic salt of peroxide of iron is reduced to a protoxide salt.

The ingredients of the copperas-vat are—Water; pure or previously purified green vitriol; indigo reduced to a homogeneous and impalpable creamy paste;

and lime of good quality, slaked just before use, and sifted. The reaction of these substances upon each other takes place in the cold, but is greatly aided by a moderate elevation of temperature. It is not possible to give precise practical instructions as regards the proportionate quantities of each of these materials to be employed, because these vary in almost every dye-works, and in many instances they are trade secrets. When the vat is to be used for plain dyeing, it is usual to take the quantities of lime and copperas in excess of what is indicated by theory, because by proceeding thus there is formed an excess of hydrated protoxide of iron, and enough lime is left to serve the purpose of again reducing and re-dissolving any indigo which becomes oxidised and insoluble. This proceeding is greatly promoted by stirring up the contents of the vat, as is usual after some pieces have been dyed. The following examples may serve the purpose of exhibiting the proportions of the ingredients employed by dyers in setting vats:-Indigo, I part; crystallised sulphate of iron, 3 parts; carefully slaked lime, 3 parts. Some dyers prefer to employ a larger quantity of lime than of sulphate of iron, and make the mixture-Indigo, 2 parts; crystallised sulphate of iron, 5.5 parts; lime, 6.5 parts.

When white indigo is intended to be used for printing, the following mixture answers the purpose:—Indigo, 1 part; sulphate of iron, 2 parts; lime, 3 parts;

but these proportions do not answer well for dyeing.

We stated, upon the authority of Berzelius, that an excess of lime is injutious, and tends to occasion a considerable loss of colouring matter, because the white indigo can—while combining with lime in a higher proportion—form an insoluble basic body, which, by settling to the bottom of the vat along with the rest of the sediment, becomes lost for the purpose of dyeing. Although the correctness of this statement need not be doubted, he has overrated its practical bearing, because the practical experience of M. E. Schlumberger, who purposely studied this point on the large scale, does not agree with this statement of the eminent Swedish savant. It often happens that in practice on the large scale matters differ from laboratory experiments, and Berzelius is quite correct in recommending to avoid an excess of lime and sulphate of protoxide of iron, because it increases the bulk of the sediment without any real advantage.

As regards the method of making the mixture, this also differs in different dye-works. The most rational plan is to mix the indigo in a pasty state with the milk of lime, and next to add gradually, and while the contents of the vat are being stirred, the solution of copperas. By following this plan, the white indigo, while being gradually formed, is at once dissolved by the excess of lime: but when the quantity of substances is rather large this method is difficult of execution, on account of the contents of the vat becoming very thick and pasty, and difficult to stir at first, and it is therefore preferable to mix the indigo with the solution of the green vitriol, and to add the milk of lime next gradually. The operation, to be successful, requires only a small quantity of water; the milk of lime should be used freshly prepared and still warm, owing to the heat developed while the quick-lime is being slaked, and the green vitriol is best dissolved in hot, or even in boiling, water. After the mixture has been made it is left quietly standing for several hours, care being taken to stir the liquid occasionally. As soon as the liquid becomes an olive-

yellow the reduction is complete, and the vat ready for use. According to Schwartzenberg the liquid contains in solution reduced indigotin, some indigored, and all the gluten, with a trace of the brown matter. The sediment contains the whole of the indigo-brown combined with lime, the greater part of the indigo-red, some gluten, a very small quantity of indigotin, sulphate of lime, and hydrated peroxide of iron. The same author states that indigo-red does not sensibly affect the dyeing process, but that this assertion is an error is known to all practical blue dyers who have used qualities rich in red colouring matters.

The vats in large dye-works are oblong cisterns, made of flag-stones large enough to form the four sides and the bottom, so that there are joints only at the corners. They are 9 feet long, 3½ wide, and 9 deep.

In many dye-works small tanks (tubs) only are used, the size being such as only to suit a piece of goods of some 50 metres in length: these tanks are constructed of wood, the shape being cylindrical. The piece or pieces of goods to be dyed are stretched on a peculiarly constructed apparatus, consisting of a wooden pole, bearing at each of its ends another piece of wood, shaped as a star, with six or eight arms; one of these is made movable by means of a screw: the arms are provided with hooks, on to which the goods are fastened. When small tanks or tubs are used this arrangement admits of readily transferring the wooden framework containing the goods from one tank to another.

Some manufacturers of colours precipitate the indigotin from old vats, and employ it again in making up new vats. This operation is conducted as follows:-The clear liquid as well as the sediments of the vats are, by suitable means (pumps or other contrivances), poured over into very large wooden tanks, and therein diluted with a large quantity of water; sulphate of iron and lime are next added, in such quantities as to cause the reduction, as well as complete solution, of all the indigo present, a laboratory assay being made of the old vat residues, so as to have some guide to the quantity present and to the ingredients required to be added. The contents of these tanks are thoroughly stirred, and next left to settle; the clear liquid is made to run in thin layers over shallow wooden troughs, so as to expose as much surface of liquid as possible to the action of the air; hydrochloric acid is added, and the precipitated blue indigo is collected on filters, consisting of woollen blankets stretched in suitably constructed wooden framework. The sediment left in the tanks is repeatedly treated with water, and some lime and sulphate of iron are also added, and thus the indigo is as much as possible recovered.

Calico, linen yarn, linen thread, and hemp yarn or thread, are always dyed, if with indigo, by means of the cold green vitriol vat: a simple immersion in the vat is sufficient to produce, after proper exposure to air, a uniform blue colour; and by varying the strength of the vat, and the length of time of each immersion, it is possible to obtain, as may be desired, a series of shades from the very lightest sky-blue to a tint so deep as to appear nearly black. The length of time allowed for the immersion of the goods has a great influence on the quantity of indigotin which becomes fixed. The tissue attracts by its pores indigotin, and this attraction is the cause that the vats become exhausted of colouring matter long before all the liquid which serves the purpose of keeping the dye-stuff in solution is absorbed.

Since it is of the highest importance that the dyed goods should be evenly coloured, it is, in the first place, best to moisten the goods first uniformly with water, and it is next very important that the goods should be very uniformly fastened and stretched on the frames, and very uniformly pressed on emerging from the vat; lastly, inequalities in the exposure to air are to be avoided. As a rule, the time of exposure to air should be precisely the same as that of the duration of immersion in the vats, and that operation may vary from five to fifteen minutes.

The fastness and uniformity of the shades is promoted by operating gradually,—that is to say, beginning with immersion in weaker vats, and going by degrees to stronger, whereby the penetration of the indigotin into the centre of the fibres is rendered more complete. The tissues to be dyed ought to be very well bleached and very clean, since any fatty matter or dirt which may adhere acts as a resist, and thus prevents uniformity of shade. After dyeing and exposure to air, the goods are passed through a bath containing dilute sulphuric acid (sp. gr. 1'007 to 1'013), in order to remove any carbonate of lime which has been precipitated by the carbonic acid of the air, and also to act as a clearing. They are next washed in pure cold water, and

Vat-dyed blue goods are considerably improved in appearance by being passed through hot milk of lime, or by treatment with alkalies, whereby, in all probability, some yellow matters are eliminated. It is on this account

that such goods are frequently passed through a soap-bath.

Vat-dyed goods, consisting of fibres of vegetable origin, may be combined with white or otherwise coloured patterns, which can be done by two entirely distinct processes:—In some instances there is printed on the goods, previous to blue vatting, a preparation technically called a resist, or reserve, whereby the fixation of indigotin is prevented upon the spots where such preparation is deposited; in other instances, again, the indigotin of the uniformly bluedyed goods is removed by suitable means, viz., chemical compounds on such portions of the cloth as are brought under the influence of these substances.

This proceeding is termed a discharge method.

The resists are either such as act mechanically only by preventing the penetration of the indigotin into the fibre, - in this way wax and pipe-clay act, -or they exert a chemical action, setting up an energetic oxidising action which causes the oxidation of the indigotin before it has had time to reach the fibre. Such is the mode of action of salts of copper and of bichloride of mercury; but the reader should bear in mind that this classification does not apply rigorously, because we are acquainted with many substances which act simultaneously as mechanical resists and chemical discharges; the copper salts, for instance, while oxidising white indigo and precipitating on the tissue a thin layer of blue indigotin (viz., in the vat itself), cause thereby the formation of a more or less impermeable layer, that layer being the blue indigotin, which, however, does not adhere to, neither is in any way fixed on, the fibre. The salts of zinc and aluminium, which are frequently employed, furnish simultaneously a deposit of white indigo and a gelatinous envelope, consisting of the hydrated oxide of either metal. The following materials act more or less in a similar manner:-Arsenic acid, acid arseniates and phosphates, boracic acid, salts of lead and of peroxide of iron. Copper and lead soaps act simultaneously as chemical and mechanical resists. In practice, however, the various substances mentioned are suitably mixed, and so blended together as to make the result satisfactory.

The reader will find below instances given of the mixtures in actual use. The thickeners play in themselves a great part in this matter, and it is of the highest importance to understand the mode of action of every thickener and the proportion which should be mixed with the resist compound: it is clear, therefore, that the making of a good resist depends on understanding the various quantities of the constituents of the resist, calculated as well in reference to the strength of the vat as to the depth of shade to be reserved. It is a main condition that a resist should become hard immediately on the goods being immersed in the vat; if the resist becomes soft, the consequence is that the colour runs. The acidity of the resist mixture should therefore be in proportion to the alkalinity of the vat: a strongly acid resist, which would harden readily in a strongly alkaline vat, would soften and run in a feebly alkaline vat: on the other hand, again, a nearly neutral resist, which might do for a weak vat, would be useless in a strong one. It is clear, therefore, that the choice of this or that salt or base is far from indifferent in this matter: sulphates and nitrates are stronger resists than acetates, which latter, in their turn, suit very well for weak vats. The most generally used white resist is made up of pipe-clay, gum, verdigris, and sulphate of copper: the goods to be dyed blue with a white pattern (white resist) are commonly not strongly bleached, but simply boiled in soda-lye, because in that state they are better and more rapidly dyed. Such goods are, moreover, submitted to another operation previous to being immersed in the vat; they are passed through a weak, very fluid, starch paste, to which some sulphate of copper and nitrate of ammonia are added, with the view first to render the pieces uniformly moist, and next to promote oxidation as well as the penetration of the indigo. After this operation the goods are lightly dried and calendered; next, the resist is printed on; the fabric again dried, and after that vatted. The fabric is next cleared in a weak solution of tepid sulphuric acid, sp. gr. 1.013.

When the resist, instead of being applied to a white ground, is printed on to a piece already blue dyed, the result will be the production of a light blue

design upon a deep blue ground.

When a piece of goods has been arranged so as to leave, after vatting, white portions, it is clear that on these portions there may be printed steam-colours, or even a mordant, and that the piece so prepared may be treated as if the whole of it were white, the result, after dyeing, being the production of a piece upon which several colours may be present on a blue ground. This kind of work requires a very nice adjustment of the engraved cylinders. If, instead of an ordinary white reserve, there is employed a composition which contains acetate or nitrate of lead and a salt of copper, the result will be that by vatting a portion of the oxide of lead becomes fixed; when, after the vatting, the fabric is first immersed in dilute sulphuric acid, and next in milk of lime, and afterwards dyed in a bath containing a saturated solution of bichromate, with or without lime, the final result will be the production of a yellow or orange pattern. When this resist is printed on previous to bluevatting, and the piece afterwards dyed in bichromate, there will be produced a green-coloured pattern surrounded by deep blue. Again, a reserve may be

employed which contains the elements of the red mordant: after ageing, the piece is vatted, next washed in a running stream, and after that dyed in madder, the result being the production of a red pattern on a blue ground.

These instances prove the great variety of patterns which can be produced. The details of these operations are entirely matters of practice, requiring very nicely adjusted mechanical arrangements. The following are receipts for different resists:—

For Deep Blue.—Water, 4 litres; sulphate of copper, 1.25 kilos.; acetate of copper, 500 grms.; nitrate of copper, 875 grms.; alum, 240 grms.; pipe-clay, 2.125 kilos.; calcined starch, 1.25 kilos.

For Medium Blue.—Water, 4 litres; sulphate of copper, 500 grms.; acetate of copper, 250 grms.; nitrate of copper, 500 grms.; alum,

240 grms.; pipe-clay, 2 kilos.; calcined starch, 1 kilo.

Red-Resist, so-called Lapis.—Red liquor, sp. gr. 1.07, 12 litres; Senegal gum, from 2 to 3 kilos.; pipe-clay, 4 to 6 kilos.; olive oil, 1 kilo.; sulphate of copper, 1 kilo.; nitrate of copper, 500 grms.; salammoniac, 1.5 kilos.

White Lapis.—No. 1: Lime juice at a sp. gr. of 1'109, 5 litres; thickened lime juice, thickened with 1'5 kilos. of gum upon 2 litres, 1'5 litres; sulphate of copper, 1 kilo.; pipe-clay, 3 kilos. No. 2: Water, 2 litres; sulphate of zinc, 1 kilo.; pipe-clay, 725 grms.; gum Senegal, 500 grms.; solution of nitrate of copper, sp. gr. 1'52, 0'12 litre.

For White Under Mordants, and for Blue Contours.—Caustic soda solution, sp. gr. 1.070, 8 litres; arseniate of potassa, 3.5 kilos.; corrosive sublimate, 500 grms.; pipe-clay, 3 kilos.; gum Senegal,

1.5 kilos.

The so-called discharge method is in many respects rather inconvenient; it does not admit of very finely engraved patterns; and it requires very strong vats to prevent the running of the discharges. The application of the latter is always preceded by dyeing the goods uniformly blue, the strength of the vats being of very little importance in this process. The employment of discharges is based upon the property of energetic oxidising substances, whereby the indigotin is converted into soluble isatin. The most generally applied discharge is chromic acid, but since that substance cannot be used in a free state, because it will be immediately acted upon by the thickener, which would convert it into chromic oxide, a circuitous process is used. Upon the woven tissue bichromate or neutral chromate of potassa is padded, and when dry there is printed on the pieces a composition, chiefly made up of an acid, whereby the chromic acid is set free; the strength of the chromic acid solution must be regulated according to the intensity of the blue colour previously imparted to the cloth. A medium blue requires an almost saturated solution of the chromate; the goods padded with bichromate cannot be dried in the open air, at least not by direct exposure to sunlight, because that would cause the destruction of much of the indigo. Oxalic acid is very commonly employed as the chief constituent of the paste intended to set the chromic acid free; it is thickened with gum, dextrin, or starch, to which some pipeclay is added; in some instances nitric, sulphuric, or tartaric acid is applied. The decolouration of the portions of the blue colour of the cloth, where the acid composition has been fixed, is almost instantaneous; the goods are next washed in warm water, wherein chalk is kept suspended, thereby to saturate the excess of acid.

Instead of employing as discharges the salts of chromic acid just named, chromate of lead is sometimes applied, being printed on with a suitable thickener, and, after having become dry, the goods are passed through a rather strong solution of moderately warm hydrochloric acid. In this case it is not so much chromic acid as chlorine set free, which acts as a discharge and decolourises the indigo. Instead of chromate of lead hydrated peroxide of manganese is sometimes applied.

of manganese is sometimes applied.

M. Mercer discovered that a mixture of red prussiate of potassa (ferricyanide of potassium) and caustic potassa or soda would discharge indigo-blue in a very perfect manner; but on account of difficulties in the application and of the costliness of this process it has not been much employed. If the materials be mixed and printed on a blue the colour is at once discharged, and only requires washing off; but the mixture has a very energetic action upon all thickening matters, and is very irregular in its results; on the other hand, it does not impair the strength of the fibre. The discharges upon indigo-blue can be made to act as mordants, or colours to produce a coloured design instead of a white one. For example, if acetate of alumina be mixed with the discharge, and the alumina fixed in the washing off, it may be dyed up in madder or garancin to produce a coloured discharge. Sometimes the discharge and resist are combined together; for instance, on light blue ground are printed simultaneously in the first place an ordinary resist, and, secondly, the same resist, to which has been added bichromate of potassa and hydrochloric acid; when the fabric so prepared is again vatted the result will be a deep blue ground, whereon is a pattern of light blue and white.

In order to give an idea of the composition of the materials used for discharging indigo-blue we quote the following:—Chrome liquor consists of—Water, 2 litres, wherein are dissolved 500 grms. of yellow chromate. The acid composition contains—Tartaric acid, 3 kilos.; oxalic acid, 250 grms.; calcined starch, 4 kilos.; nitric acid, 500 grms.; water, 4 litres. This last composition is printed on by rollers; the wet pieces, rolled up between a loosely-woven cloth, are immersed momentarily in water, and as soon as white becomes apparent

are placed at once in tepid water containing chalk.

Before we proceed to consider the combinations of other colours which may be formed by the aid of the vat-dyed materials, we give here a short outline of what has been said on dyeing with indigo:—The usual method of dyeing cotton self blue is to fill with water large stone or wooden tanks, and dissolving therein 2 parts of sulphate of protoxide of iron, adding 1 part of finely-ground indigo, and 3 parts of hydrate of lime. After having stirred the whole well for several hours, pieces of calico which have been hooked on a frame and dipped in lime-water,* in order to moisten them equally all over, are plunged for some fifteen minutes into the vat, when the blue indigo which has been converted into white indigo by the protoxide of iron, and rendered soluble by the excess of lime, fixes itself on the fibre, and on the latter being afterwards exposed to the atmosphere re-absorbs oxygen, and becomes blue. When white patterns are required the pieces are printed before dyeing with what is

^{*} This is often used in preference to ordinary water, in order to make sure that there be excess of lime.

called a "reserve" or "resist," that is, a composition which prevents the colour from fixing itself on the fibre; the chief ingredient for that purpose is sulphate of copper, which acts by prematurely oxidising the indigo, and thus prevents its fixation. In both cases the pieces are passed through a weak sulphuric acid bath to insure the perfect fixation of the indigo. Formerly the copper thereby liberated from the fabrics was completely lost, but Mr. J. Leese devised, some years ago, a method of saving this metal; to effect this, the diluted solution of sulphate of copper is made to filter through vessels containing wrought-iron turnings; the acid dissolves the iron, which may be used as sulphate of protoxide of iron for future operations, whilst the copper deposited may be used again either to prepare sulphate of copper or utilised in another manner. As an instance of the importance of small savings, it may be stated that by this ingenious but apparently trifling improvement one firm alone saved at least £3000 a year.

Dr. F. C. Calvert effected, some years ago, an economy in this branch of calico printing and dyeing, consisting in extracting from the cold indigo-vats, which were considered to be exhausted, a certain percentage of the indigo originally employed. Dr. Calvert observed that a green insoluble flocculent matter, which was considered by chemists and printers to be simply oxide of iron, was in reality a compound of indigo and iron. In order to recover this he devised the following simple method:—The green pulp is conveyed from the exhausted vats into a general receptacle, and there mixed first with a small quanity of hydrochloric acid, so as to remove the excess of lime, allowing the green pulp to settle and running off the liquor. The green pulp thus purified is next treated with strong hydrochloric acid, whereby chloride of iron is produced and indigo liberated, which, after having been washed with water, is again fit for use.

Although in a later portion of this chapter more details will be given on printing with indigo, we give here the following brief outline, which is one of great difficulty, but successfully carried out by various methods: -That usually employed consists in mixing very finely powdered indigo with orpiment or protochloride of tin and a caustic alkali, a process which is further facilitated by printing the pieces in an atmosphere of coal-gas, as first devised by Mr. Bennett Woodcroft, and carried out by Messrs. T. Hoyle and Sons, of Manchester. Of late years Mr. J. Leese, of the firm of Kershaw, Leese, and Co., has succeeded in applying the following method, first devised by Fritzsche: -The indigo is ground to an impalpable powder, and then mixed with glucose, lime, and caustic soda, in such proportions as are needed to produce the shade required. These materials are all mixed cold, and the cloth when printed is passed through a steam chest, wherein it is exposed for from 30 to 60 seconds. In this short period the indigo is completely reduced, and thereby rendered soluble in the alkalies. It enters, penetrates, and combines* with the fibre. On emerging from the steam chest it becomes oxidised and fixed by exposure to the atmosphere; or the pieces may be immersed in a solution of an

^{*} According to a series of experiments made in Java, the results of which have not been made public, by the late Dr. Fromberg, aided by Dr. Croockewit and other scientific and practical men, vegetable fibres, also wool, silk, and hair, are not only penetrated by porosity through the fibre, but actually enter into chemical combination with the white indigo, and form a definite compound therewith.

oxidising agent, such as dilute sulphate of copper, after which they only require to be washed, dried, and finished.

Indigo is frequently applied in combination with other dyes, the object being the formation of green and other shades; the combination of the indigo-blue and chrome-yellow producing the so-called vatted green. This operation requires four tanks; the contents of the first tank consist of a solution of 2 litres of subacetate of lead, of sp. gr. = 1'421, and a limewater, made up of 2.5 kilos. of lime with water, to form a liquid of a sp. gr. = 1'020; the second tank contains pure water; the third tank is a cold indigo vat, with 7'5 kilos. indigo; the fourth tank contains a liquid, made up of 5 kilos, bichromate of potassa and 40 litres of vinegar. The operation of dyeing is carried out in this manner: the goods or pieces are plunged for three minutes in the first tank, rinsed in the second, next plunged for five minutes in the third tank, and next rinsed in the fourth, wherein the indigo is oxidised, and simultaneously the green dye brought out. The goods are then washed in running water, next immersed in another bichromate bath, again washed in cold water, after which the cloth is passed through a cold caustic soda bath, containing for each piece a litre of caustic soda solution at a sp. gr. of 1.070. After another wash the goods are dried and are ready for packing when they have been calendered. In this way an even and uniform green is obtained. If an acid discharge is printed thereon, and the goods washed, and then, if desired, immersed in a solution of bichromate of potassa and lime, the result will be the production of a white pattern, or also of a yellow on a green ground.

Another kind of green ground is produced by mordanting previously vatted cloth with acetate of alumina, and dyeing the so-prepared fabric next with quercitron, yellow berries, or weld; if instead of quercitron madder is employed a very beautiful puce is produced. Not only the colours just mentioned, but a great many others, can be fixed on a previously-vatted and subsequently-mordanted cloth. Goods which have been first dyed with peroxide of manganese (manganese brown) possess the remarkable property of taking up a far larger quantity of indigotin than they would take up if vatted while white; the result is the production of a black ground, whereupon it is possible to bring out white, brown (bistre colour), and blue designs, either in discharge or resist styles. Thus there may be formed: a bistre ground, whereupon a resist having been printed gives after vatting a black ground and bistre designs; or bistre ground, whereupon is next printed a discharge for white (an acid tin-salt), yielding after vatting a black ground, whereon are blue patterns; the same result is obtained when upon the black ground (that is to say, indigo-blue after and over bistre) a bistre discharger (viz., simply a weak acid, which does not act upon the indigo) is printed. A bistre-brown ground, with resist for blue, and simultaneously a discharge for brown, yields white; this effect is also produced by printing an acid (stronger) on the black, in which case the peroxide of manganese causes the oxidation of the indigo. i.e., its decolouration, while the former is simultaneously decolourised, becoming converted into a soluble proto-salt of manganese. Combinations of indigo and hydrated oxide of iron yield similar results, but are less easily managed, and are not so beautiful.

What has been mentioned above concerning vat blues applies chiefly to

calicos. Since linen and hempen tissues possess, generally speaking, less affinity for dyes, some precautions are also necessary when they are to be dyed with indigo by the self blue or vat process. These goods are, therefore, previous to vatting, either first passed through a thin starch pastel, to which some salt has been added, or through weak lime-water, but rarely or never are these goods printed, and the process is, therefore, simply one of uniform blue dyeing.

As regards the application of indigo to woollen fabrics, these are always vatted, and, in fact, a very large proportion of woollen cloth is grounded by means of the indigo vat; more frequently woollen and worsted yarns than woollen woven fabrics are vatted, but if the latter are thus treated it is only

a plain blue dye they receive, and no resists are applied.

According to general ideas prevailing among woollen dyers in this country, the lime and copperas vat is not well adapted for woollen goods, and the usual blue vat is made up in a different manner, viz.—Water, 500 gallons; indigo, 20 lbs.; potash or soda, 30 lbs.; bran, q lbs.; madder, q lbs. The water is heated to near its boiling-point; the potassa, bran, and madder are first introduced, and then the indigo previously very finely ground; cold water is added to bring the temperature down to 90° F., and the vat is kept at that heat all through; the ingredients are very well stirred every twelve hours, and the vat should be ready for use in forty-eight hours after settling. This vat does not work longer than a month, and is somewhat expensive on account of the loss of potash. Another vat, much more manageable and lasting, since it may be worked for two years without emptying, being freshened up as required, and known in France as the German vat, is made up of 2000 gallons of water, heated to 130° F.; 20 lbs. of crystals of soda, 21 pecks of bran, and 12 lbs. of ground indigo are added, and then the mixture well raked up; in twelve hours a fermentation sets in, bubbles of gas arise, the liquid has a sweetish smell, and has become greenish; 2 lbs. of slaked lime are now added, the liquid well stirred, the vat heated again, commonly by the aid of steam, and covered up for twelve hours, when a similar quantity of bran, indigo, soda, and again a little lime are added; in about forty-eight hours after the setting the vat may be worked, but because the reductive power of bran is rather feeble, an addition of 6 lbs. of molasses is made. If the fermentation becomes too active, it is repressed by the addition of lime; if too sluggish, it is stimulated by the addition of bran and molasses, and, like all other blue vats for wool, is worked hot. In France, however, the copperas and lime vat is used for wool also, though not exclusively.

Silk is rarely, if ever, dyed blue by the aid of the lime and copperas vat; in fact, generally speaking, the textile fibres of animal origin are dyed by means of so-called pastel, woad, urine, and Indian vats. The reduction of the indigotin is, in all these instances, the result of a peculiar fermentation called into existence in an alkaline liquor by the aid of substances containing much nitrogen, and also by the aid of suitable carbohydrates (sugar, &c.). We know that under these conditions sugar is rapidly converted, provided the temperature be sufficiently elevated, into butyric acid, while carbonic acid and hydrogen are simultaneously set free: the latter substance combines in the nascent state with the indigotin, and the white indigo is rendered soluble in the alkali present in the liquid: the fermentescible carbohydrates are derived from bran, madder, and sometimes molasses; the nitrogenous matter

is obtained from the pastel or woad, which is sometimes added in large quantity to the liquid in the vats; this substance then also yields the indigotin it contains.

In those vats wherein pastel is not employed the nitrogenous matter is derived from the bran: sometimes putrefying human urine is employed, for the sake partly of the alkali it contains (viz., carbonate of ammonia), and also for the organic nitrogenous matter, which acts as a ferment, while the former plays the part of a solvent for the white indigo.

Since the phenomena attending fermentation are of a complex nature, even in the most simple instance, it cannot be wondered at that, in such an instance as is here given, there is not—as regards the success of the process on an industrial scale—that certainty which attends the working of the lime copperas-vats, and only a long practice and a lucky empiricism make sure of success in a method which, scientifically considered, is not by any means fully elucidated. It is on this account that the details which follow on this subject are less extensive as to theory.

Pastel-vats, rarely employed in this country, vary in size from 2 to 2.5 metres in diameter by 3 metres depth. The ingredients employed are 100 kilos. of pastel, in the shape of balls; the vat or tank is next filled with tepid water; after which there are added 10 kilos. of madder,* 3 to 4 kilos. of bran, and 4 kilos, of slaked lime, well mixed with water to a thick creamy liquid; sometimes also weld is added: this mixture is left standing for eight hours, after which time the contents are thoroughly raked up, an operation which is repeated every three hours: gradually a peculiar ammoniacal smell is given off, and the surface of the liquid in the vat becomes covered with a bluish scum, under which deeper blue-coloured veins are seen. Since these symptoms indicate that the indigotin of the pastel has become dissolved, there is added to the vat a quantity of 10 kilos. of finely-ground indigo, previously mixed to a paste with water. If the fermentation becomes too active, as evidenced by the size and quantity of the gas given off, it is moderated by the addition of a small quantity of lime, while, if it is too feeble, it is quickened by the addition of bran. A pleasant odour, neither too strong nor too weak, and abundance of blue scum, are the signs of a proper condition of the contents of the vats. The fabrics which are first immersed in a freshly-made up vat are less beautifully dyed than those done afterwards, because the wool withdraws from the bath some drab, brown, or yellow matters, which are the result of the reaction of the various substances contained in the vat on each other. The woollen goods, either pieces or yarns, are kept immersed in the vat for two hours, after which time they are aired, and next washed: roo kilos. of wool consume from 8 to 12 kilos. of indigo; it is therefore evident that this loss or consumption of indigo has to be restored after each day's work, and this is done by adding every night a sufficient quantity of indigo along with some lime. After having been thus kept up for some months, the vat, becoming gradually foul, is exhausted,-that is to say, the dyeing process is continued until no more colour is imparted to the wool; after which the contents of the vat are run off, the tank cleaned, and a fresh vat made up.

Another kind of vat is made up in the following manner: -8000 litres of

^{*} Madder in this case is only employed as a substance rich in sugar, and also because it contains some nitrogenous matter.

water and 200 kilos. of pastel are heated to 95° C. by the aid of steam; after some few hours there are added 6 kilos. of indigo, 8 kilos. of madder, 2 kilos. of bran, 4 kilos. of lime, and 4 kilos. of potash (pearl-ash): this mixture is stirred up every three hours during the first forty-eight hours after having been made: when the reduction of the indigo goes on well, there are still added 6 kilos. of indigo and 1 kilo. of madder. The contents of the vat are next stirred up from time to time, and then left at rest till the next day. The temperature of the vat is kept up at from 40° to 50° C.; after each day's work there is added to this vat a quantity of 1.5 kilos. of madder, and every third day 6 kilos. of indigo. When this vat is once put into proper working order it lasts for several months.

The so-called Indian, or potash vat, employed for dyeing wool and silk, is made up with bran, madder, indigo, and potash; the indigo is only added to the mixture of water, and the other ingredients after they have been heated up to 90° C.; afterwards the temperature is kept up to between 30° and 40° C., the mixture being thoroughly stirred up once in every twelve hours for a period of forty-eight hours. The colour of the liquid should be a greenish-yellow with a coppery hue, and bluish-coloured scum on the surface. The quantities employed are—Indigo, 8 kilos.; potash (pearl-ash), 12 kilos.; bran and madder, each 3.5 kilos. In order to keep up this vat there are added to it, when required, certain quantities of alkali, indigo, and madder. This kind of vat is more readily managed, not so easily spoiled, and works quicker, -that is to say, it is possible to dye three times as much wool in it in the same time, and, moreover, the dyed fabric does not, on being washed in soap, cast off so much superfluous dye as with the pastel-vats; but this alkali-vat has to be refreshed about every twenty-five to thirty days, because the potash becomes soon saturated with the fat and grease of the wool.

More advantageous than the Indian is the vat generally known as the German, employed not only in that country, but also elsewhere. To the water, having been first heated to 95° C., are added 20 pailfuls of bran, 11 kilos. of carbonate of soda, 5.5 kilos. of indigo, and 2.5 kilos. of lime just slaked previously, while the temperature is kept up at from 40° to 50° C.: fermentation sets in after about twelve hours; the liquid gives off a somewhat sour smell, becomes coloured a greenish-blue, and gives off gas-bubbles: from time to time the same quantities of indigo, soda, and lime are added, and, moreover, some 3 to 4 kilos. of molasses: the vat is fit for use after the third day. Since soda is much cheaper than potash, this vat is more economical for that reason. The German vat may last, in good working order, for fully two years.

The fermentation indigo-vats are subject to diseases, which are more especially to be feared with the pastel-vats. The more frequently occurring diseases are due either to an excess or to a deficiency of lime: in the first-named instance the colour of the liquid becomes more and more clear and bright, the bluish scum decreases, and the odour disappearing, fermentation stops, and the active principles are precipitated: when this defect is discovered in good time, it is remedied by the addition of sulphate of iron. In case there happens to be a deficiency of lime, the fermentation becomes first too active, and next enters the putrescent stage. The liquid turns red, and, if vatted cloth is plunged into it, it is soon decolourised. The only remedy for this disease is to heat the liquid to 90°, and to add lime; if this does not arrest the

process at once, the vat is lost, and the contents have to be run away. The mode of working these vats is as follows:—They are stirred up first thing in the morning, when the scum is also removed from the top; then, in order that the goods to be dyed may not touch the sediment at the bottom, there is placed in the liquid a net, made of thin strong twine, fastened to a wooden hoop: the goods are dyed, immersed in the vat, inside this net; the time of immersion varies, but is generally from twenty to twenty-five minutes. When withdrawn from the vat the goods appear greenish-yellow, but very soon become blue on exposure to the air. The immersion is repeated as often as is needed to produce the desired shade. The goods are afterwards washed, first in acidulated water, next in a plentiful supply of clear water.

Silk is always dyed in the Indian vat, but, since the blue is never very deep, Prussian blue or the aniline blues are preferred, though indigo has the advantage in fastness.

M. Leuchs* has suggested to do away with all the vats above mentioned, and to utilise instead the property of pectin and pectic acid of reducing indigo in presence of soda. Products containing these pectic compounds are very common in the vegetable kingdom, and the turnip tribe yields them in abundance. The suggestion is valuable, but has never been tried in practice, except on a very limited scale. A large manufacturer in Belgium reports, in a private communication, that when you have intelligent workmen this process is excellent, but the prejudice of foremen stands in the way of its general adoption, the fact being that they think no good can be done with cheap materials,rubbish as they term it,—as are turnips, mangolds, beets, and the like. Specimens of woollens and silks vatted in this manner are not only not inferior, but, according to competent judges, superior to those done in the common vats. In some exceptional cases the kind of vat above described as German is used for cotton piece-dyeing; this is principally for thick and heavy goods, into which the cold lime and copperas liquor-vat would not penetrate sufficiently well.

An entirely new vat has been proposed by Messrs. Schützenberger and Lalande. Bisulphite of soda, standing at 30° to 35° Baumé, is brought in contact in a covered vessel with twisted sheet zinc or granulated zinc, filling up to the top of the vessel without occupying more than one-fourth of its real volume. After the lapse of about one hour the liquid is poured into an excess of milk of lime, which precipitates the salts of zinc. It is stirred, and the clear liquid drawn off either by filtration and pressure, or by decantation after the addition of water. Air should be excluded as much as possible. By mixing the hydrosulphite thus obtained with ground indigo and the amounts of lime or soda needful to dissolve the reduced indigo, we obtain at once a yellowish liquid containing no insoluble matter except the earthy impurities of the indigo. One kilogramme of indigo may be thus reduced so as to form a solution not exceeding 10 to 15 litres in volume. For dyeing, a certain quantity of the reduced indigo solution is run into a vat filled with water. This vat being clear in its entire depth, the operation of dyeing involves no loss of time. The excess of hydrosulphite constantly reduces the scum of oxidised indigo forming on the surface of the dye-bath, the strength of which can be kept up during working by successive additions of the concentrated

indigo solution. Thus the required shade can be obtained with the smallest possible number of dips. This vat gives shades more solid and clear than can be obtained with the old vats, and enables the dyer to produce upon wool very light blue bottoms, which are ordinarily got by means of sulphate of indigo, and are in consequence much more fugitive. The authors propose to print with an alkaline solution of reduced indigo, suitably concentrated and thickened, containing a large excess of hydrosulphite of soda. The presence of this salt tends to keep the indigo-blue reduced, which otherwise tends to become oxidised during the time of printing. This part of the process can be carried out in common air, and with an ordinary machine, the oxidation being so slight that after an hour's work the remnant of the colour is still yellow and soluble. By thus printing on reduced indigo immediate fixation is secured, and the entire colouring matter is utilised. Experience has proved that, for equal shades, 50 to 60 per cent less indigo is consumed with the new process than with the old. The shades obtained are more beautiful and solid, and the impression is better defined. The new indigo-blue, requiring no subsequent fixing process, can be printed along with a great number of other colours, such as aniline black, garancin, colours obtained by dyeing or steaming, catechu shades, chrome colours, colours fixed with albumen, &c. Thus new styles may be created which would be difficult to execute in any other manner. The blue printing colour is formed by thickening, with gum or any other suitable material, a sufficiently concentrated solution of white indigo in an alkali, and adding to the mixture a sufficient quantity of hydrosulphite of soda. After printing, the pieces are hung up for twenty-four hours to oxidise, washed, and soaped.

We have now to consider the methods of fixing indigotin in printing, a process solely applied to calico. The pencil-blue style dates back certainly ninety or a hundred years, and no improvements have been made upon it since the commencement.

Pencil-blue consists of reduced indigo, and is made by heating a mixture of finely-ground indigo, orpiment, and potash. These latter substances form a powerful deoxidising mixture, which speedily reduces and dissolves the indigo. In a short time after mixing, the blue colour of the indigo disappears, and gives way to a yellow, except at the surface, where the oxygen of the air continually revives the indigo, causing it to assume a coppery-blue. The avidity of this mixture for oxygen, whereby the indigo is restored to its blue insoluble state, is so great that it cannot be exposed a moment to the air without being covered with a scuni or pellicle of blue indigo, and it is also the cause of the great difficulty in applying pencil-blue in a regular and satisfactory manner. As soon as the block or roller leaves the colour, and enters the air, the surface of the colour is covered with a scum of indigo, which, being insoluble itself, cannot enter the fibre of the cloth, and, lying on the surface of the soluble colour, is a hindrance to its entering into the fibre. Peculiar arrangements have to be made in applying this colour to prevent contact with the air; they are all more or less defective, and the results are often irregular. In the old method of applying it with a pencil, the pressure upon the fibres of the pencil (this consisted of a piece of willow-wood stick, which, by means of a blow given with a mallet on one of the ends, was somewhat split and splintered into a

fibrous mass) containing the blue could drive the film of indigo aside at the very moment when the pure colour beneath could enter into the cloth and unite with the fibre; but in either block or roller printing* the cloth and design are perpendicular to each other, and the face of the colour comes in flat contact with the cloth: the insoluble particles, being deposited first, hinder and prevent the fixation of the others. Many ingenious constructions of reservoirs and sieves for block printing have been made specially for this colour, and, with the exercise of great care, it has been possible to print with some of them, and obtain tolerably uniform results; but they have not admitted of general application.

There is less especial difficulty in printing pencil-blue with the cylinder. Thousands of pieces are weekly printed in America, and a considerable number here. The apparatus used is a "doctor-box." The blue oxidised layer of colour is removed, and the engraved portions of the cylinder work in the green solution last, and go thence at once to the cloth.

As an instance of the mode of making up a mixture for pencil-blue, we quote the following for dark blue:—10 gals. indigo-pulp, containing 40 lbs. indigo; 40 lbs. yellow orpiment; 11½ gals. soda-lye, at 70° Tw.; 18½ gals. water; 4 lbs. lime. Boil till yellow when spread on glass; let settle, and thicken the clear with 120 lbs. gum Senegal.

We have already referred to Bennet Woodcroft's process, bearing upon the production of a good dark blue by means of the rollers. The patentee, acting under the knowledge that it was the oxygen of the air which—both on the roller and on the colour—was the obstacle to neat and proper printing, proposed to construct covered apparatus to surround the colour-box and roller, and to receive the piece when printed; and in all these spaces where the air was in contact with the colour, he proposed to expel it by introducing common coal-gas from the gas-mains, since, as a rule, this gas does not contain any oxygen, or at least only a very small percentage,† it could not act upon the colour, which it was supposed would then have a fair chance of entering the

^{*} The difference between block printing and roller or cylinder printing consists in the fact that while the block (generally a square piece of wood, upon one surface of which the desired pattern is either cut en bas-relief, or is executed in a peculiar style by means of copper wires projecting very slightly from the surface of the block) not only deposits the colour upon the cloth, but to a greater or less extent forces it in, the cloth in cylinder printing (the cylinders are made of copper, upon which the pattern is engraved) has to absorb the colour, partly by capillary attraction and partly by the pressure of the lapping. The same colours do not answer indifferently for block and roller styles. Block-colours can be worked usually thinner (i. e., require less thickening—the reader should also bear in mind that the term colour is often used in cases where really only a mordant is printed) than cylinder, or so-called machine-colours, and it is possible to apply colours by block which could not well be applied by cylinder. Among such colours are those containing insoluble matters, like pipe-clay, sulphate of lead, &c. For heavy shades upon woollen cloth (flannel printing) the block has undoubtedly the advantage over the cylinder, because not only does wool demand much more colouring matter than cotton to produce a shade of equal depth, but it does not absorb it so quickly, since its fibres are less readily wetted than those of cotton, and it consequently does not receive colour from the engraving in sufficient quantity. Dark blues, chocolate-browns, greens, &c., on the finest class of French woollen cloth, require to be blocked two or three times to receive sufficient colour for full heavy shades.

⁺ It is not the place here to enter into details on this matter; but the fact is that, unless under very exceptional conditions, gas manufactured on the large scale is never quite free from some air.

cloth. The idea was good, but notwithstanding large sums of money have been spent to give this process a fair trial, requiring as it does complicated machinery, it has signally failed. Some of the causes of this failure are quite unaccountable, so that the process was abandoned in despair, and has never been worked for the last eighteen years.

We have now to turn our attention to an application of indigo known as China blue, because the blue colour had a similarity to the well-known blue of old China ware. It is produced by a process so extraordinary in its results that it is impossible to conceive how or where it originated, and although this application of indigo has now become obsolete, we cannot be justified in omitting to enter into some details on this subject.

The theory of China blue printing is exceedingly simple: the indigo, reduced to an impalpable powder, is thickened, and this mixture is printed on by means of cylinders or blocks. After drying, the goods exhibit a more or less deep blue pattern, according to the quantity of indigo employed; but this blue would not resist even a rinsing in cold water. The next stage is therefore to reduce and dissolve the indigotin on the spot, and thereby to cause it to penetrate and combine with the fibre to be definitively fixed after a process of oxidation. These operations have to be performed so as to preserve the sharpness of the design and prevent any colour from running. The following means are resorted to: - The cloth is first passed through a tank containing milk of lime, next through one containing a solution of sulphate of iron, next through a solution of soda, and, lastly, through weak sulphuric acid, which, while dissolving the oxide of iron, causes the precipitation of the white indigo, and aids also its oxidation. This is only an outline of the method to illustrate the theory; the practice is essentially different, so as to secure success. In the first place, the printer begins his operation with the preparation of standard colour in the following manner: - He takes 4 kilos. of very finely-pulverised and sifted indigo (for this special purpose the Caraccas indigo is preferred, because, although it is less rich in colouring matter than Bengal or Java indigo, it is more readily pulverised, and can be obtained in a powder as fine as the finest ultramarine); acetate of iron, 10 litres; sulphate of iron, 1 kilo.; water, 10 litres; Senegal gum, 6 kilos.: this mixture is well stirred and passed through a sieve, and whenever it is required for use, it is first well stirred. This standard colour serves to prepare the following colours, which are employed for being printed on the cloth :-

Colours to be applied by roller or cylinder, beginning with
the lightest and proceeding to the heaviest shades

Standard blue; parts

Acetate of iron liquor, at 7° Baumé (sp. gr. 1°048), containing
700 grms. of gum per litre

Gum-water, made up of 600 grms. to the litre

1 2 3 4

2 1 1 2 1

These shades may be varied in different ways, according to the desired pattern. Since the indigo has a tendency to settle to the bottom of the vessel from which it is supplied to the rollers, the liquid contained in that vessel has to be stirred about now and then. If it happens that the pattern consists of more than one blue, the machine-printer has to take care that—after the first colour has been printed on and dried—he does not give too much colour to the subsequent patterns, whereby the underlaying might become re-dissolved.

INDIGO.

After printing on all the patterns, the cloth is kept for some time before undergoing other processes, in order to give time for the oxidation of the acetate of iron, whereby the indigo is made to adhere more firmly, and the risk of its becoming detached from the cloth, when the latter is immersed in the tanks, is prevented. If this precaution is neglected, the shade becomes unequal. Six tanks are employed in this process,-viz., two lime tanks, each containing 12.5 kilos. of slaked lime; one copperas tank, at a strength of 7° Baumé (1.048 sp. gr.); one tank containing caustic soda (sp. gr. 1.101); a tank containing 500 grms. of strong sulphuric acid to each pailful of water; and, lastly, a tank with good fresh water. The goods are left for a quarter of an hour in the first lime-water tank, care being taken to impart to the piece a slight movement upwards and downwards; next, the pieces are immersed in the copperas tank, and left therein quietly for a quarter of an hour; next, another quarter of an hour in the second lime tank; and after that again a quarter of an hour in the copperas, followed by a stay of five minutes in the caustic soda, and half an hour in the dilute sulphuric acid, wherein the pieces are thoroughly moved about and rinsed, and from this bath they are lastly transferred to the clean water bath. After the passing of each piece through the lime-water tanks, there is added to each of these 2 kilos, of freshly-slaked lime, while 50 kilos, of copperas are added to refresh the tank of this material after ten pieces have been passed through it. The soda tank is kept in working order by the addition of about 4 kilos, of caustic soda after the passage of every five pieces. The tank containing the sulphuric acid is kept up by the addition of 25 kilos. of acid after five pieces have been passed through, while, moreover, the contents of this tank are thrown away as soon as it is dirty, a freshly-filled supplementary tank being in readiness.

The experience of M. E. Schwartz, of Bâle and Mulhouse, has proved that, in order to make this method of working successful, the soda ought to be thoroughly caustic, and kept up at the above-quoted strength, while it is also essential that the copperas solution should be neutral, for which purpose the solution is boiled with some clean scrap iron. After the goods have been washed in the fresh-water tank, they are thoroughly washed in a current of water, and next left over night in a very weak solution of sulphuric acid (sp. gr. 1007), in order thereby to remove the last traces of peroxide of iron. The next morning the goods are again washed in cold water, and afterwards passed through hot soap-water (temperature 50°).

So-called China green is obtained by adding to the colour mixture some bichloride and nitro-muriate of tin. The blue colour is fixed as above described, but the goods are only left for two minutes in the soda and five minutes in the acid tank. After washing, the pieces are dyed with quereitron.

Very dark shades cannot be obtained in the China blue style: it is a fast colour, but expensive, on account of the time and labour it requires, especially if carried out by the old process of dipping the goods attached on frames: by the more modern method, described above, the vats (tanks) are supplied with rollers, and the pieces passed through quickly; time is saved, but it is at the expense of the quality.

A resist for China blue, if required, may be obtained by thickening a mixture of sulphate of copper, acetate of lead, nitrate of copper, and lime-jaice.

Fast blue and green colours are now produced upon calico (printed on) by a

process which in some respects is similar to, but in others different from, China blue. This method consists essentially in the employment of a mixture containing white indigo, along with another substance which serves to prevent the too rapid oxidation of the white indigo. The compound is prepared as follows:-The clear liquid of a strongly-made copperas vat is precipitated with acidified solution of protochloride of tin; the precipitate-indigotate of hydrated protoxide of tin-is collected on filters made of a woollen fabric, care being taken to protect the same as much as possible from contact of air. A better preparation is obtained by heating a mixture of indigo, caustic soda, and protochloride of tin, and precipitating it with hydrochloric acid; the pasty mass thus obtained is thickened with gum, and frequently some tin-salt is also added, to guard against every possible chance of oxidation before the mixture is printed on to the cloth, while as soon as it is brought thereon the white indigotin ought to be rendered soluble, to make it penetrate the fibre. This last condition is readily obtained by passing the cloth at once into milk of lime, which causes the immediate decomposition of the tin compound, the lime combining with the colouring matter, the colour of which changes from pale greyish-white to apple-green; the white indigo becomes indeed soluble for a moment, but the presence of an excess of lime and of the thickener, aided by the affinity of the fibre, prevent the colour from running. After being withdrawn from the lime tank, the goods are washed in running water, when the oxidation begins at once, and with it also the fixation of the dyeware, which becomes completed by the immersion of the goods in dilute sulphuric acid. If to the colour, previous to use, a proto-salt of iron is added, the oxide of which is precipitated in the lime tank, and if, instead of a simple acid bath, to such a bath be added yellow prussiate of potassa, the tint of the indigo-blue, which by itself is always a bright, not deep, blue, is very considerably deepened: instead of milk of lime a hot carbonate of soda bath (sp. gr. 1.070) is employed, while instead of the sulphuric acid bath a solution of bichromate of potassa is employed. The goods are left for five minutes in the soda solution, and next rinsed for the same time in the second solution; after which the goods are washed and soaked for an hour in a running stream. The cloth is next washed in hot soapsuds (70°).

The fast green is obtained by adding to the indigotate of tin mixture any suitable lead-salt (acetate commonly), which is first converted into oxide of lead in the soda-bath, and next into sulphate, in the sulphuric acid bath. This sulphate, being converted into a chromate by immersion in a solution of bichromate of potassa, produces, with the blue of the indigo, a fast and solid green.

Mr. Ward patented, in the year 1857, a method of employing indigo which has obtained the name of glucose blue: the indigo, in the blue insoluble state, is mixed with a deoxidising material, preferably grape sugar or glucose, and an alkali, soda or lime. This mixture, technically called the colour, is applied cold to the cloth, and as soon as the goods leave the printing machine, and without drying, they are passed into steam for about a minute. The heat of the steam causes the reaction to take place, viz., the reduction of the blue indigotin, which, being converted into white indigo, is in that state dissolved by the alkali, and enabled to enter the fibre of the woven tissue, which next requires washing and oxidising to bring up the blue colour. This

process does not appear to have been ever extensively carried out: the intention was that it should be applied in combination with madder, the mordant for the latter being printed on at the same time.

A practical printer of great experience informs us that, setting aside the very serious difficulty of steaming the goods before they are dry, whereby they are exposed to many and serious accidents, the patentee's process, as published in his specification, would have to be greatly modified before it could be practically applied.

M. E. Schlumberger has thoroughly investigated the subject of fixing indigo by the so-called steaming process. He tried the following method:—Starting with the knowledge that hydrated protoxide of tin reduces indigotin in the cold, provided an alkali be present, he found that if, instead of the alkali, cyanide of potassium be employed, the indigotin becomes only soluble (and of course first reduced) during the steaming. The following mixture was tried:—

Indigo-paste (that is to say, indigo ground to pulp with) water), containing 20 per cent dry indigo	16 parts
water), containing 20 per cent dry indigo	1
Best cyanide of potassium (in cakes)	16 ,,
Wet pasty hydrate of protoxide of tin	16 ,,
Gum-water	52 ,,

This colour was found too expensive, and had the disadvantage of running too readily, and could not be printed on simultaneously with any colours giving off acids. It was never M. Schlumberger's intention to introduce this colour on the large scale, but he found that it is capable of producing a most magnificent fast green on being combined with cadmium yellow, prepared according to M. Sacc, by means of a hyposulphite. This green resists, without alteration, all the operations of madder dyeing.

When indigo-dyed calico is treated with a strong solution of caustic alkali, the shades of colour become deeper, in consequence of the contraction the tissue undergoes.

Indigo-dyed fabrics are recognised by their exhibiting a somewhat dull blue colour, which resists the action of alkalies and of all acids which do not—by acting as oxidising substances—destroy the colour. Among these acids the nitric and chromic are the more common. Chlorine-water destroys the blue colour of indigo. A freshly-made solution of zinc in sulphurous acid also decolourises indigo.

When vatted tissue is immersed in a hot alkaline solution of protoxide of tin it becomes decolourised, and the liquid turns blue on exposure to air. When a vatted tissue is treated with the strongest fuming sulphuric acid the fibre is destroyed, but if the liquid be diluted with water and filtered a blue liquid will be obtained, exhibiting all the characteristics of the so-called Saxon blue.

We have now to turn our attention to the application of the sulphuric derivatives of indigo. Sulphindigotic and sulphopurpuric acids have no affinity whatever for vegetable fibres, not even after they have been animalised or albuminised. When even the so-called Saxon blue is occasionally applied to cotton, after the excess of sulphuric acid has been saturated with either acetate of lead or acetate of soda, whereby an equivalent proportion of acetic acid is set free, and a preparation formed which is erroneously called acetate

of indigo, this application takes only place for goods which are not to be washed, the blue tinge imparted being not fixed at all.

Woollen and silk fibres do not behave in the same way with sulphindigotic and sulphopurpuric acid: the direct affinity of sulphindigotic acid for animal fibres is limited by certain conditions. When an excess of alkali is present with this acid, or even when it is in the state of a neutral salt, it does not dye wool, and this is readily explained by the facts above stated, as alkalies extract the colour from wool, this process being made use of in the preparation of so-called distilled blue. Although sulphindigotic acid unites directly with wool, this property of the fibre is increased by the use of such mordants as alumina and oxide of tin. The dyeing with the substance just ramed should always be executed in presence of an excess of acid, since the greater that excess the greater the brilliancy of the hue, and the more quickly the process is finished. In former days the so-called Saxon blue, a solution of indigo in sulphuric acid, diluted with water, was used; now-a-days indigo-carmine is employed, while for printing on wool the so-called acetate of indigo above mentioned is preferred.

The dyeing of the wool with indigo-carmine is very readily effected in a warm bath, containing the carmine, alum, and sometimes also cream of tartar. The alum enhances the solidity and fastness of this blue.

When the colour produced upon wool has been obtained by means of a sulphindigotic acid prepared with a large excess of fuming sulphuric acid (viz., more than twelve times the weight of acid to that of indigo), such blue imperfectly resists treatment with alkalies, and even repeated washing with soap, especially if during the dyeing operation heat be applied to the liquid in the dye-beck.

Silk is dyed in a precisely similar manner, but it is first alumed. Sulphindigotic acid forms the ground colour for many mixed shades, as, for instance, green, grey, violet, and black; it is largely used in its modern form of indigocarmine, because it is so readily fixed. The printing operations are conducted in a manner similar to that of dyeing: the solution of indigo-carmine is slightly acidulated with oxalic acid, thickened with gum, alum being sometimes added in small quantity. Indigo-carmine is also largely employed for the production of such colours as green, violet, grey, and it is added to a number of others to alter their tone.

Indigo-blue, that is to say the indigo-carmine and sulphindigotic acid, is readily detected upon wool or silk by the following tests:—A moderately strong and tepid solution of crystalline carbonate of soda dissolves the blue colour, the liquid becoming blue-coloured. Chlorine, nitric, and chromic acids destroy the colour, as do also concentrated caustic soda, and a freshly-made solution of zinc in sulphurous acid; on the other hand, this dye is not acted upon by sulphuric, hydrochloric, and the stronger vegetable acids. According to M. C. Kœchlin,* indigo-purple is violet when printed, but becomes blue after having been steamed, and remains so, owing to the action of the sulphurous acid which the woollen tissue retains from the brimstone vapours to which it is exposed in bleaching.

We end this account of indigo with a brief statement of the mode employed

[&]quot; Bulleun, de la Societé Industrie, le de Mulhouse," vol. xviv., p. 335

INDIGO.

by the Chinese for dyeing blue. They designate all the plants they are acquainted with, and which yield indigo, with the word lan, while the blue colour derived therefrom is called lan-tien; they employ the fresh leaves of at least five different species of plants for dyeing blue in the following manner:

—The fabric to be dyed is thoroughly cleaned in pure water, and, after having been dried, the cloth is steeped into a tepid warm bath, containing the leaves of the lan, to which some lime-juice is added.

CHAPTER VI.

BROWN AND BLACK COLOURING MATTERS. ASTRINGENTS.

WE have now to treat of a class of proximate vegetable products which are colourless by themselves, only yielding brown, grey, or black tints under the influence of a special oxidation, or by the action of peculiar mordants; most of these substances belong to a class of organic compounds as yet not thoroughly known.

Under the common name of cutch, catechu, gambier, cashew, and terra Japonica there are met with in trade several kinds of vegetable extracts, obtained by exhausting certain parts of plants, and evaporating the liquid thus obtained to a suitable consistency. Several varieties of this substance are distinguished in commerce according to the country of their production, the species of plant they are derived from, and the form in which they are brought into the market. The following are the chief varieties:*-Genuine catechu, terra Yaponica vera, is obtained from the internal portion of the wood of the Acacia catechu, a tree belonging to the Leguminosæ, section Mimosæ. This tree, which attains a height of from 5 to 7 metres, is a native of Bengal and other parts of Hindostan, and the islands of the Indian Archipelago. In order to obtain the catechu the tree is cut down while it is fullest of juice, the soft white coloured splint-wood is torn and cut away, and the internal portion of the tree having been sawn into small sticks is boiled in water, in vessels made of unglazed pottery; the liquid so obtained is concentrated first over an open charcoal fire, and next placed for evaporation in the sun in shallow dishes until the desired consistence has been obtained. The extract thus prepared yields three varieties of brown catechu, viz.:-

- a. The cutch on leaves, so-called Pegu catechu, met with in the trade in cakes, weighing from 35 to 40 kilos., packed in large leaves; a dry, glossy, brownish-red, or blackish-brown substance, of uniform texture throughout, and of a sp. gr. 1.39.
- b. Brown cutch run into moulds, made in the sand or clay, is a less pure and inferior article.
- c. Brown catechu, in cubic-shaped cakes, packed in coarse bags, weighing from 35 to 40 kilos. per cake; this kind of cutch is imported from Java, Singapore, Pegu (via Calcutta), chiefly into the ports of London, Amsterdam, and Hamburg.

The Bengal cutch is obtained by a process similar to that just described,

[•] Guibourt, "Journ. de Pharmacie," (3), xi., 24, 260, 360; xii., 37, 183, 267. Girardin, "Leçons de Chimie," 4th edition, ii., p. 636.

KINO. 491

from the fruit of the areca palm, Areca catechu, a tree widely spread over the tropic portion of Asia. This kind of cutch is met with in commerce in the shape of cubical blocks, each side measuring from 3 to 4 centimetres. The colour of this substance is brighter than that of the cutch which is shipped at Bombay (the mixed produce of the Acacia catechu and areca nut), the colour being chocolate-brown, with deeper and lighter coloured bands alternating. This substance exhibits a dull appearance when broken, and is very dry and sandy, although sand is not necessarily present; the sp. gr. is 1.28.

Yellow cutch, cubical cutch, or gambir, is the extract obtained from the leaves of the *Uncaria gambir* and *Uncaria acida* shrubs, belonging to the family of the Rubiaceæ, tribe of the Cinchonas (Roxburg), abundantly met with in Sumatra, Malacca, Pulo-Penang, Singapore, the Moluccas, and the Sunda Islands. This kind of cutch, known very generally as gambir, occurs in commerce in the shape of thick flat cakes, externally brown, internally

bright yellow, fracture dull, taste bitter and astringent.

Kino or gum kino, the produce of the Butea frondosa (Leguminosæ) and the Ptericarpus marsupium, also of some other plants, is a deep blackish brown, glossy-looking substance, of an astringent and bitter taste, only used in medicine. The following preparation of kino might be worthy of practical investigation:—Boil powdered kino for some time in water. On cooling the concentrated solution a substance separates out, and is collected upon a filter. It is then boiled in concentrated hydrochloric acid, when it dissolves with an intense violet colour. This is allowed to cool, and then diluted with water, when a rich dark brown powder is deposited, and carefully washed. It is soluble in alcohol with a violet-red, and in hot acetic acid with a poppy-red. The latter solution is said to give a pale rose shade on stuffs mordanted with salts of iron. It dyes wool and cotton moderately, and silk very finely. With tin mordants it yields rich cherry and scarlet shades; alumina compounds are unfavourable to the colour.

As regards their chemical composition, the above-named substances do not differ much from each other. By qualitative tests there have been found in

these substances the following matters:-

r. A peculiar kind of tannin, soluble in cold water, precipitated by gelatin, and also by salts of the peroxide of iron with a greyish-green colour; not precipitated by a solution of tartar emetic. This rather ill-defined body, whose properties and composition are not very well known, is termed catechutannic acid.

 A colourless, crystallisable principle, called catechuin or catechuic acid, which is the main cause of the tinchorial properties of catechu.

 Brown so-called extractive substance, present in greater or less quantity, and due to the alteration of the two foregoing matters.

Catechutannic acid is an amorphous, colourless substance, soluble in cold water, as well as in alcohol and ether; its taste is astringent. It may be prepared in an impure state by adding to a cold-made and concentrated aqueous solution of catechu concentrated sulphuric acid; the precipitate thus produced is washed with water slightly acidulated with sulphuric acid, and next re-dissolved in water; this solution is treated with carbonate of lead, filtered, and concentrated in vacuo. Another mode of preparation consists in treating catechu, coarsely powdered and put in a displacement apparatus,

with ether; the solution thus obtained yields, on evaporation in vacuo, a porous vellowish mass.

According to Dr. Delfts,* the solution of catechutannic acid becomes, when exposed to air, deep red, and yields then catechuin; this latter assertion is denied by M. Neubauer,† who states that the oxidation of the catechuin caused by exposure of its solution to air results in the formation of a tannin precipitable by gelatin.

Alkalies favour the oxidation of the tannin of catechu when in aqueous solution; catechutannic acid does not yield glucose when it is boiled with dilute sulphuric acid, and differs in that respect from ordinary tannin, viz., that of nut-galls.

According to the researches of Dr. Davy and Dr. Nees von Esenbeck, the quantity per cent of catechutannic acid found in the undermentioned varieties of catechu amounts to:—Bombay cutch, 54.4; Bengal, 48.2; Gambir, 36 to 40.

Catechuin, when pure, is a silky crystalline substance, with a peculiar mother-of-pearl-like appearance, containing water of crystallisation, driven off at 100°; fusing at 217°, decomposed at a higher temperature, and thereby converted into a volatile product, pyrocatechuic or oxyphenic acid, C₆H₆O₂. Catechuin is almost devoid of taste, neutral to test-paper; soluble in 1133 parts of water at 17°, and in from 2 to 3 parts of boiling water, but crystallising from that solution on cooling in acicular-shaped crystals; soluble in from 5 to 6 parts of cold, and from 2 to 3 parts of hot, alcohol; soluble in 120 parts of cold, and from 7 to 8 parts of boiling, ether.

Catechuin is best prepared from the yellow catechu met with in cubicalshaped cakes; this substance, first reduced to powder, is next exhausted with cold water for the purpose of eliminating the tannin; the residue is then treated with about eight times its weight of boiling water; the catechuin separates from this solution after cooling, and the substance is then pressed between cloth to separate the mother-liquor; thereupon the crystalline mass is re-dissolved in water, and this solution precipitated with subacetate of lead. Care is taken to add this reagent drop by drop, and to stop further addition as soon as a white precipitate begins to appear; the fluid is then filtered, and the filtrate precipitated with the above reagent. The deposit thus thrown down is washed with some hot distilled water, and next suspended in boiling water, and decomposed by means of sulphuretted hydrogen. The liquid is again filtered while yet hot, and on cooling deposits pure catechuin. This substance consists, in the anhydrous state of 61.4 per cent of carbon, and 5 per cent of hydrogen, the remainder being oxygen; in the hydrated state it contains per cent-Carbon, 52.06; hydrogen, 6.0.

In consequence of the importance of catechuin as a dye-stuff, we have to enter into some details here on the different opinions held in reference to the composition of this material. M. Zwenger proposes the formula C₂₀H₁₈O₈; M. Neubauer prefers C₁₇H₁₈O₇. According to Dr. Strecker, catechuin is a

Neubauer, "Ann. der Chem. und Pharm.," xcvi., 337.

^{* &}quot;Jahresb. für Prakt. Pharm.," xii., 162.

[†] The following are the most important papers on this subject, published in the periodicals:

Nees von Esenbeck, "Ann. der Chem. und Pharm." i., 343. Zwenger, "Ann. der Chem. und Pharm." xxxvii., 326. Delfts, loc.cit.

Neubauer, loc. cit. Van Delben and Kraut, "Ann. der Chem. und Pharm.," xxxvii., 285. Schützenberger and Rack, "Bullet, Soc. Chimiq. de Paris," July, 1865, p. 5.

mixture of two very closely allied homologous substances, which can be separated from each other with great difficulty, viz., deutocatechuic acid, $C_{16}H_{16}O_8$, and tritocatechuic acid, $C_{18}H_{20}O_8$. Kraut and V. Delben, again, do not share Dr. Strecker's opinion, and propose for catechuin the formula $C_{12}H_{12}O_5+2H_2O$; Hlasiwetz and Malin prefer $C_{19}H_{18}O_8$; and the following formulæ, $C_{10}H_{10}O_4$ and $C_{22}H_{22}O_9$, also agree with the results of the elementary analysis. It is clear, therefore, that the true formula for catechuin can only be settled by deduction from the products derived from it, and to these derivatives we have now to turn our attention.

When catechuin is boiled with dilute sulphuric acid, with exclusion as much as possible of air, or boiled with alcohol, previously saturated with hydrochloric acid gas, it is converted into a brown amorphous body, insoluble in water and alcohol, catechuretin, which appears to be formed by dehydration from catechuin; the formulæ assigned to catechuretin are, according to M. Neubauer, $C_{17}H_{14}O_7$; Kraut and V. Delben, $C_{12}H_{10}O_4$; Hlasiwetz, $C_{19}H_{14}O_6 = C_{19}H_{18}O_3$ (catechuin) minus $_{2}H_{2}O$, also $C_{22}H_{18}O_7$.

When catechuin is fused with hydrate of potassa it is split up into phloroglucin and protocatechuic acid, a reaction which Hlasiwetz represents by—

 $C_{19}H_{18}O_8 + O_2 = C_7H_6O_4 + 2C_6H_6O_3.$ Protocatechuic Phloroglucin.

Catechuin yields with bromine-water an insoluble reddish matter named bromo-catechuretin, the formula of which is, according to Kraut and V. Delben, C₁₂Br₄H₆O₄, or C₁₉H₈Br₆O₆, according to Hlasiwetz and Malin. Chloride of benzoyl yields, when heated to 190° with catechuin, two new products, one of which, soluble in alcohol, appears to be monobenzoic catechuin, while the other body, insoluble in alcohol, seems to be benzoic catechuretin. When catechuin is heated to 100° with hydriodic acid, the organic substance is deoxidised and transformed into a yellow elastic granular body, insoluble in water, alcohol, ether, and acetic acid; containing in 100 parts 63.90 carbon, and 5.0 of hydrogen, the remainder being oxygen. A solution of catechuin in acetic acid yields, upon the addition of pulverised binoxide of barium a white body, insoluble in boiling water, soluble in acetic acid, and precipitated from that solution in a crystalline state upon the addition of water; the percentage composition of this body is-Carbon, 58.0; hydrogen, 4'70; the rest being oxygen. Catechuin is converted by bichromate of potassa as well as by dilute and hot nitric acid into a brown insoluble amorphous body; that resulting from the action of bichromate of potassa consists, in 100 parts, of-Carbon, 58.07; hydrogen, 3.42; the rest being oxygen. This brown matter is readily soluble in dilute nitric acid, the result being the giving off of carbonic and the formation of oxalic acid. With concentrated nitric acid, catechuin yields a product analogous to picric acid. Catechuin absorbs oxygen very rapidly and completely in presence of alkalies, and such solutions become the reby first red, then brown, and contain in that condition some brown, ill-defined substances known as rubinic and japonic acids. Catechuin undergoes the same alteration when its aqueous solution is exposed to air, but the action is more slow; it is this reaction and property of catechuin, viz., its readily yielding by oxidation brown insoluble matters, which is the basis of its application in dyeing and printing.

When the crude catechu of commerce is exposed to a temperature of 100°, it fuses, becomes transparent, losing from 4 to 5 per cent of its weight of water; on ignition in a platinum crucible, there is left from 3 to 4 per cent of mineral incombustible matter. Catechu being an extract, is liable to be adulterated with various other substances, among which sand, clay, ochre, dried blood, sugar, and coarse starch are the chief; the careful examination of the physical and organoleptical characters of the substance, as well as of the quantity and nature of the residues insoluble in water and alcohol, the quantity and nature of the ash, may give some idea of the purity of the sample, which ought to be entirely soluble in hot water, and then give a brown, not blackish, solution. It ought not to be totally soluble in cold water, for that is an indication of heating and partial decomposition. The hot, watery solution should, on cooling, deposit a portion of the catechu in a fine, granular state. The only reliable test for the quality of catechu is to make some colour from it, or to dye up samples from it in comparison with an equal weight of a known sample.

Catechu is employed* in medicine, for tanning skins, and for dyeing. For this latter purpose, catechu has been used in India from time immemorial. It was not employed in Europe until in 1806, when MM. Schæppler and Hartmann first used it as a brown colour in conjunction with madder work. Their method of application described by Dr. Dingler + was, however, not adopted; and catechu was hardly used for dyeing or printing to any extent until 1829, when M. Barbet, of Jouy, re-introduced it. Catechu yields, when boiled with water, a furbid decoction; the infusion above named is commonly also turbid: but when there are added to the water 8 parts of vinegar (sp. gr. 1.007, containing 4 per cent of anhydrous acetic acid), and the boiling continued for some time, a rather clear solution is obtained. Catechu is also readily soluble in caustic soda lye of moderate strength. An aqueous decoction of catechu yields, with calico mordanted with alum, a deep yellow, and with iron mordants an olive. This shade becomes brighter and far more beautiful by the addition of glue; while by being passed through a solution of bichromate of potassa, the shades of both mordants are made brown. When a small quantity of acetate of copper is added to the decoction of catechu, it yields with alumed calico a kind of oak-brown colour, and with an iron mordant a deep cinnamon-brown. If the solution or decoction of catechu is acted upon by a solution of bichromate of potassa previous to being fixed upon the cloth, it becomes unsuitable for use.

Generally speaking, catechu is of no use for dyeing purposes unless the oxidation takes place upon the tissue itself; indeed, the colourable matter present in cutch (the catechuin) is only soluble and capable of penetrating into the fibres as long as it is not oxidised, for when once the oxidation of catechuin has taken place, it becomes totally inert and insoluble, and is then only capable of being mechanically fixed. The processes by which colours derived from catechu are obtained are based upon the following principles:—The catechuin is applied in solution on the fibre which is penetrated

^{* &}quot;Bulletin de la Société Industrielle de Mulhouse," vol. xii., pp. 354, 373; vol. xiii., p. 291; vol. xiv., p. 197.

[†] Dingler's "Polyt. Journ.," ii., No. 1, 1815. This mixture is printed on the calico, is next steamed, and afterwards passed through a solution of bichromate of potassa.

by it, and the woven tissue is next placed in such a condition as is most expedient for the oxidation, and, consequently, transformation, of the colourable principle into a brown insoluble and firmly-adhering substance. The oxidation can be effected by:—

- Exposure of the tissue to air,—a rather slow process,—with the simultaneous application of steam.
- 2. The transformation is greatly accelerated and aided by the introduction into the colour mixture of such materials as are capable of acting as oxidating substances either more slowly or more rapidly if steam is applied; such substances are in this case salts of copper.
- 3. The oxidation is greatly accelerated by passing the tissue after the catechuin—that is to say, the catechu, since as yet pure catechuin is not commercially prepared in a state of chemical purity—has been printed on, into an alkaline solution, whereby the affinity of the catechuin for oxygen is greatly increased.
- 4. By passing the goods through a solution of bichromate of potassa.
- Lastly, a combination is made of two of these processes, viz., steaming and passing into bichromate, or also ageing and steaming.

It has been suggested to wash powdered catechu in cold water, which dissolves the tannin, leaving catechuin untouched. This latter substance, being soluble in hot water, is then fit for use. Sace states that catechu, when treated with sulphuric acid, is decomposed chiefly into glucose and a brown resin, which, on being dissolved either in moderately strong sulphuric acid, or in an alkaline solution, assumes a beautiful purple colour remarkable for its stability. The brown resin is probably employed by some dyers and printers in place of catechu. Of course, if catechu alone is used, the manufacturer applies the most rapid and complete method, which is undoubtedly the passage through bichromate; but if it is mixed up with other colours, it is requisite to adopt the process which suits the case, so as to have the desired effect upon the catechu, yet not to injure or alter the other colours.

The natural tint which catechu produces is modified by the introduction or addition of divers metallic salts, such as those of iron, manganese, and others, among which the salts of copper play an important part, chiefly, however, for the fixing of catechu. This point has been purposely investigated by MM. C. Koechlin and Mathieu-Plessy.* As a result from their experiments, confirmed by those of M. H. Schlumberger, we learn that sal-ammoniac has a specific influence in promoting the oxidation of the colourable matter of cutch by the oxy-salts of copper; indeed the oldest receipts for the employment of catechu, given by Schæppler and Hartmann in 1806, and by M. Esslingerat Jouy in 1829, recommend the mixing of a salt of copper and sal-ammoniac as a means of fixing the dye upon cloth.

The mode of action of the sal-ammoniac is differently explained. According to M. Persoz, it acts by its tendency to form double salts, thereby keeping in solution divers salts and oxides; according to Schwartz, the sal-ammoniac should serve to prevent the catechu from combining with gum. The latter idea is of little value, the less as the same mixture is usefully employed in other instances for the very purpose of causing oxidation, as in the

^{* &}quot;Bulletin de la Société Industrielle de Mulhouse," vol. xxii., p. 311 and following.

case of red woods, logwood, and aniline black. M. Kæchlin thinks that the sal-ammoniac acts by double decomposition, causing the formation of chloride of copper, which in its turn is converted into protochloride by the catechuin, and together kept in solution by the sal-ammoniac. The last-named salt, by becoming again oxidised by contact of air, is again capable of acting upon a fresh portion of organic matter: the sal-ammoniac cannot be replaced by any other ammoniacal salt; and although M. Kæchlin states that chloride of sodium acts in a similar manner, this is denied by Schlumberger, who purposely tried it experimentally. Recently it has been found that sulphuret of copper can be advantageously used instead of the oxy-salts of that metal.

About the year 1832 the fixation of cutch by means of the bichromate was first applied by MM. Kochlin Frères, at Mulhouse. The deeper-coloured goods are steamed before they are padded in the chromate solution, which should be sufficiently strong to prevent the colour running, while the solution is made warm. For bright-coloured goods the steaming is simply replaced by an exposure to air.

The oxidation of the catechuin in the bichromate solution is instantaneous, producing at once a brown colour; the chromate solution itself is reduced to sesquioxide.

M. Schlumberger thinks that there is a kind of chrome-lake formed along with the oxidised catechu, the oxide entering into combination and modifying the colour produced. M. Heckmann* states that some of the oxide is only mechanically mixed with the colour, and this is the generally admitted opinion.

Oxidation by means of passing the goods through milk of lime is another process, which, although less satisfactory, is employed whenever catechu is printed on along with such colours as are fixed by means of lime, as is the case with fast blue. The presence of an alkali or of an alkaline earth aids the absorption of oxygen by the catechuin, but this operation is usually carried out along with the employment of salts of copper and of sal-ammoniac, and also with the ageing process.

Catechu serves for dyeing bright and deep brown, fawn, drab, and wood colours, and also for printing. Catechu colours are often associated with garancin colours, by mordanting with alumina and dyeing up in garancin and cutch, the hue produced is modified, and turned to brownish-red.

The cutch dyes are remarkable on account of their fastness; they resist alkalies, soap, acids, and even chlorine, in a high degree, and do not admit of the application of the discharge process.

Catechu is used either in aqueous deco&ion or hot infusion, or vinegar or acetic acid are mixed therewith, or a solution in caustic soda is used. The following are instances of the mode of mixing the ingredients:—

Catechu	
Soda-lye, at 10° Baumé (sp. gr. 1'070, containing about 7'75 per cent of dry caustic soda)	0.114
7.75 per cent of dry caustic soda)	8 litres.
Water	8 ,,

Thicken with gum; steam, and next oxidise by passing through a bath of bichromate (containing from 5 to 7 grms. of that salt to the litre of water), at a temperature of from 75° to 88° for two minutes.

^{* &}quot;Bulletin de la Société Industrielle de Mulhouse," vol. xiv., pp. 186 and 197.

Catechu 6 kilos	
Acetic acid, at 7° Baumé (sp. gr. 1°048, containing about 30 per cent of anhydrous acetic acid, at 15°)	•
Water 4 ,, Thicken with gum; steam, and pass through the bichromate bath.	
meken with gain, steam, and pass through the biemomate bath.	
Catechu	
Pyroligneous acid 20 litres	
Solution of acetate of lime (sp. gr. 1.048) 5 ,,	
This ingredient can only act as a hygroscopic substance.	
Solution of acetate of manganese (sp. gr. 1.246) 5 ,,	
This material modifies the hue or tint.	
Gum 7.5 kilo	S.
Again steaming, and oxidation by means of the bichromate.	
Catechu 3 kilos.	
Pyroligneous acid 6 litres	
Sal-ammoniac 360 grms	
Verdigris	
Gum-water, made up with 700 grms. to the litre 6 litres	
Acetate of lime solution	

Fabrics dyed or printed with this mixture are not steamed, and not passed through a chromate bath, but are first aged, and next passed through limewater (milk of lime).

Catechu Mixture for Madder Style.

Catechu											14 kilos.
											18 litres.
Sal-amm	onia										5 kilos.
											3'375 kilos.
Acetic ac	id (s	p. gr	. 1.0	48, c	onta	aining	g ab	out	30 p	er)	13 litres.
cent	of a	nhyd	lrous	acio	lat	15°)				- }	13 littles.
Solution	of a	etat	e of	lime							9 litres.
Gum											15 kilos.
Pyroligni	te of	alu	mina	in s	olut	ion (sp. g	r. 11	070)		I litre.

After having been printed on the tissue, along with or next to the mordant, this mixture is fixed by ageing, next passed through the dung-bath, and afterwards dyed in madder. Where it is desired to have a catechu-dyed ground four different processes may be employed:—

r. A mixture of an acetic acid decoction of catechu and pyrolignite of iron is printed on and left exposed to air for twenty-four hours, after which time it is bichromated; the decoction is made up of—

Yellow catechu		100 grms.
Water		
Acetic acid (sp. gr. 1.056,	containing 37 per cent \	100 grms.
anhydrous acid at 15°))	
Gum		r kilo.

To every 10 litres of this standard mixture 1 litre of pyrolignite of iron (sp. gr. 1.070) is taken. When the colour is to be lighter 4 litres of gum

water are added to dilute the mixture. After this mixture has been printed on, the tissue is exposed for twenty-four hours to air, and is next passed through a bath of bichromate, consisting of 5 grms. of the salt per litre of water, and kept at a temperature of 94°, this operation being carried on in a tank provided with rollers, so that the tissue is only in actual contact with the liquid for about two minutes; the goods are next washed for half an hour in the washing machine in cold water.

2. Print on a decoction of catechu, leaving out the iron preparation, and otherwise proceeding as above directed.

3. Print on the following Nankeen mordant,* consisting of—Copperas, 2 kilos.; acetate of lead, 1.5 kilos.; water, 2 litres. After the separation of the sulphate of lead there is added for every 2 litres of this preparation 1.25 kilos. of British gum; the mixture then forms the standard colour, which, according to requirements, is diluted with from 7 to 45 litres of British gum solution. After having printed this mordant on the pieces they are aged for twenty-four hours, and next passed through a silicate of soda bath, and, after having been washed, the following catechu mixture is used as dye (the mixture to serve for 50 metres):—

Water 150 litres.

Decoction of catechu, containing 180 grms. to the litre 3 ...

The temperature is gradually raised from 19° to 80°; after passing through the bichromate the goods are washed in the machine and dried.

4. Print on a red liquor, which is fixed as there directed, dye in cutch, and bichromatise.

For so-called mode grounds the following processes are employed:-

- r. A mixture of cutch and pyrolignite of iron is printed on, and the tissue next passed through a bichromate bath at the temperature of 56°.
- The above-named Nankeen mordant is printed on first, and the fabric next dyed in cutch also, as above specified, but the bichromate bath is not employed.
- 3. A mixture of catechu decoction and Nankeen mordant is printed on first, after which the fabric is aged for twenty-four hours, then exposed in a steam chest at a pressure of 30 lbs. to the square inch (2 atmospheres) for half an hour, and, lastly, washed and dried.

The same processes as those just specified are also employed for silk and wool, but the use of catechu for these animal fibres is limited to being an adjunct in some kinds of black dyeing. The browns which it yields are not so desirable as those which can be obtained from a mixture of other colouring matters and mordants.

Catechu is largely used in woollen printing (flannels and linseys) for obtaining dark shades of drab, of a red or brownish tinge, in combination with

^{*} The name of Nankeen colour is usually given to the shade of buff obtained from iron salts; in piece dyeing the cloth is run through copperas liquor, and then through lime-water; for lighter shades nitrate of iron is preferable; the colour may be softened both in appearance and to the feel by finally working in warm soap-suds; annatto gives yellower Nankeen shades, which may be combined with chrome yellow. Nankeen has obtained its name from the Chinese city Nankin, whence a peculiar buff-coloured silk and cotton were first imported into Europe. The Nankeen dyes with cutch are fast, but a great many inferior imitations exist, and have been treated of in our foregoing pages under various headings.

other colouring matters to modify the shade. Cutch yields a variety of brown shades; also olive, wood-colour, and so-called bronze hues. The applications of catechu are, however, still limited, and it is doubtless capable of many more valuable applications than it has yet received.

True Astringents.

We have now to turn our attention to some substances which are strictly astringents rather than dyes, and among these, in the first place, nut-galls. These are globular-shaped, dirty, brownish substances, having the size of small marbles, the morbid excrescences produced by the punctures of an insect called Cynips Gallæ-tinctoriæ, belonging to the order Hymenoptera, upon the leaves and young twigs of several kinds of oak trees, and more especially those of Quercus infectoria, a small tree indigenous to India, Persia, Syria, the Levant, and some parts of Greece, and other portions of the South of Europe. The fully developed nut-gall contains a central cavity, wherein, on breaking it open, will be found the larva of the insect. The galls are generally gathered and collected before the larva has had time to become fully developed, and therefore before it has consumed a portion of the internal layers of the envelope by which it is enclosed, and escaped as a mature insect. This fact is mentioned here because it bears upon the qualities of nut-galls as distinguished in commerce; the non-perforated nuts, which are heavier than the perforated, are known by the name of blue, black, or true nuts; the other kind are known as white or false nuts. The former are deemed preferable to the latter, and command a higher price, but in the English market both kinds are frequently found mixed together in the same parcel; the size and shape of the nut-galls vary, the latter being spheroidal or ovoid, and the former ranging from that of a pea to a diameter of from I to 2 centimetres. The exterior surface is more or less smooth, and with slight conical excrescences of various size. The chief commercial varieties are-

Aleppo Galls, or Turkey Galls.—Imported from Aleppo and Smyrna, whither they are brought from the interior of the country. This variety is subdivided into—Heavy black galls, of a blackish-grey colour with whitish excrescences; greenish or bluish galls, with white excrescences; whitish-yellow wrinkled and pierced (false galls).

Morea Galls.—Of the size of hazel nuts, brown, irregular-shaped, and often

Smyrna Galls.—Greenish-black, greyish-black, and whitish-yellow; are a less esteemed quality than the Aleppo galls.

So-called Marmorine Galls.—Small, round, iron-grey coloured nuts, having a smooth surface.

Istria Galls .- Very small, light, pale yellow-coloured.

French Galls.—Very small and light, smooth-surfaced, pale yellow-coloured.

Piedmontese Galls, known as "knoppern," are irregular-shaped excrescences developed upon the glands (acorns) of the Quercus pedunculata, the consequence of the puncture of an insect, the Cynips Quercuscalycis, also belonging to the order Hymenoptera. This kind of nutgall is gathered in Hungary, Dalmatia, Roumania, Styria, Piedmont, and other countries.

China Nut-galls.—More or less spherical in shape and irregular in size, externally provided with conical points, internally hollow; average size that of a Barcelona nut. This kind of gall is formed upon a species of sumac, and is highly valued on account of its large percentage of tannic acid.

Valonia Nuts, sometimes known as Levant Nut-galls, are imported into Europe from Greece, Southern Italy, Smyrna, and other parts of Asiatic Turkey; the acorn-cup of a species of oak botanically known as Quercus agilops. These cups have the shape of flowers, the acorn being in the centre, and are readily detached from the fruit by a kind of fermentation which the substance undergoes when laid up in heaps: the acorn having fallen out, the flower-like cup is dried, and is then

fit for the market.

Divi-divi, livi-divi, or libi-divi, is now one of the most important astringents in the market. It consists of the pods of Casalpinia coriaria, a small tree found in the province of Maracaibo, and in other parts of South America. The pods are of different shades of brown, sometimes nearly black; they are about 3 inches long and 1 inch broad, and are usually warped, twisted, or even doubled up. The best pods are thick and fleshy, and of a pale colour. Those which are very dark, with black spots and blotches, have probably been gathered in a damp state, or have been subsequently exposed to moisture, which greatly reduces their value. The amount of tannin in divi-divi is greater than in sumac, or even myrobalans, but it is in the first-mentioned body accompanied by a peculiar colouring principle, which limits the applications of this ware. It is very largely used in producing a black upon the cotton warps of mixed goods. Divi-divi has another defect: it is of a glutinous or adhesive nature, whence fragments of the ground pods are apt to cling to the mordanted tissues, and when washed away are found to have played the part of a resist, and protected certain portions of the goods from the action of the tannin. Consequently, when the dyeing operations are completed the cloth appears speckled. Hence it is better to extract the ware with water, and allow only the clear liquor to come in contact with the goods. Divi-divi is generally the cheapest astringent.

Myrobalans, otherwise called myrabolans, or myrabolams, are the fruit of Terminalia Chebula, a tree common in some parts of India. In shape and size myrobalans somewhat resemble shrivelled plums. They are of a pale buff colour, consisting of a dry pulp, varying in thickness, and enclosing a stone-like kernel, which contains no tannin, and forms from 23 to 52 per cent of the whole weight. The moisture present in the nuts, as found in commerce, varies from 3 to 7 per cent, and the amount of ash left on incineration is about 10 per cent. The tannic acid is mainly present in the pulp. Good unground myrobalans should be pale, plump, free from dark blotches and from wormholes. They should be hard and firm, ringing like fragments of earthenware when shaken together, and if crushed with a hammer yielding a dry, pale powder, mixed with hard irregular fragments. If they can be crushed to a dark-coloured dust between the fingers, or if they work out into a paste under the pestle, they are of poor quality. Ground myrobalans should form a pale buff powder, dry, astringent to the taste, but free from a saline flavour or from intense bitterness. If moistened and rubbed in the hand, they should form a

very tenacious paste.

The nuts, when bought whole, are often found mixed with earth, sand, mica, nux vomica, betel-nuts, &c.

Ground myrobalans are sometimes contaminated with divi-divi, spoiled sumac, and wild galls. To detect such impurities a little of the powder is thinly sprinkled over a sheet of white paper, and examined with a lens. If divi-divi has been added, fragments of its bright brown flat seeds are sure to be found. The outer skin of a myrobalan may occasionally resemble a diviseed in colour, but the minutest portion of the former shows a wrinkled surface, whilst divi-seeds are smooth. The leaf-stalks and midribs of sumac may also be distinguished, by the aid of a lens, from the torn and jagged fibre of the myrobalan.

Myrobalans, being cheaper than galls and stronger than sumac, have, to a very great extent, superseded both. Along with salts of iron, they dye cotton a fuller black than can be obtained with sumac. They are likewise preferred to sumac for fixing the coal-tar colours upon cotton, owing possibly to the fact that they contain, along with tannin, certain oily and glutinous matters. Gall-nuts and commercial tannin are, however, still preferable.

M. Muratore, of Algeria, has recently made a series of experiments with the leaves and fruit of *Pistacia lentiscus*, a tree found in various parts of Africa. He finds that the decoction gives, with salts of iron, good solid blacks upon cotton, similar to those produced by gall-nuts. With other mordants, salts, and acids, a variety of shades are obtained. The astringent principle is found also in the twigs and wood, though less abundantly than in the leaves and fruit. As to the economy of the *lentiscus* extract, as compared with other astringents, details are still wanting.

Sumac, known also as sumach and shumach, consists of the ground leaves, foot-stalks, and young twigs of several varieties of plants, technically known as sumacs, but botanically belonging to the genus Rhus, of the family of the Terebinthaceæ. The sumac of commerce is chiefly obtained from the Rhus coriaria in the following manner:—A short time before the blooming of the plant, in June or July, the younger twigs are cut off, dried in the sun, next beaten, so as to detach the leaves and flower panicles, which are next coarsely ground up by means of mill-stones. The shrub just named is a native of Asia, but is cultivated in many parts of Europe, more especially in Sicily, Spain, Southern France, and Hungary.

In the South of France a peculiar kind of sumac is prepared, and known locally as redoul or redou. It is derived from the Coriaria myrtifolia, or tanner's herb, which, according to the researches of M. Ribau, contains a violently poisonous substance known as coriamyrtin.

The leaves of the Arbutus Uva-Ursi, better known in pharmacy than in technology, are used as sumac in Dalecarlia (Sweden).

The following are the chief varieties of sumac known in the trade:-

Sicilian Sumac.—The most esteemed article, fetching always a high price Spanish Sumacs.—Exported from Malaga, Priego, or Molina-Valladolid.

Portuguese Sumacs .- From Oporto.

Italian Sumacs.

French Sumacs.

The articles are classified here according to their amount of tannin.

We have now to turn our attention to the chemical composition and other properties of the substances enumerated. Tannin, or tannic acid, is the only active principle of nut-galls, and, according to M. Guibourt's analysis, Aleppo galls contain in 100 parts—Tannin, 65.0; water, 11.5; woody fibre, 10.5; starch, 2.0; gum, 2.5; gallic acid, 2.0; ellagic acid, 2.0; brown extractive matter, 2.5; chlorophyll, sugar, albumen, and inorganic matter, 2.0.

As shown by the following figures, galls differ largely in their richness of tannin:—Aleppo galls contain, on an average, from 60 to 77'03 per cent;

China galls, 58 to 77 per cent; Smyrna galls, 33 to 60 per cent.

Tannin or tannic acid is readily prepared, in an almost pure state, from galls previously coarsely powdered, by exhausting them either with aqueous ether (9 parts of ether and 1 part of water), or with a mixture of equal parts of alcohol and ether in the first instance, in a displacement apparatus. In the lower vessel will collect two layers, the upper being ether, and the lower a syrupy solution of tannin; but if the mixture of alcohol and ether is employed as directed by M. Mohr, the fluid, after having served to macerate the galls, is evaporated to dryness.

Tannin is a whitish-yellow, amorphous, inodorous powder, possessed of an astringent taste; it is very soluble in water, less so in alcohol, and almost insoluble in ether, especially if the latter is anhydrous. When submitted to heat, tannin fuses, and begins to decompose at about 210°, giving rise to the formation of carbonic acid and pyrogallic acid, which sublimes, while a brownish residue of gallohumic acid is left. The aqueous solutions of this substance are precipitated by a great many salts, as well as acids, in consequence of the smaller solubility of tannin in such liquids.

Solution of gelatin is precipitated by tannin solution, and from the latter, if a piece of fresh skin be therein immersed, the tannin is gradually withdrawn, because the skin (the derma proper) combines with the tannin, forming what

we term leather.

Solution of tartar emetic yields with tannin a white, and per-salts of iron a deep blue, precipitate; ferrous salts do not yield a precipitate with tannin unless after lengthy exposure to air as a consequence of oxidation which has set in. With acetate of lead tannin yields a white, and with silver salts a brown, precipitate. The solutions of the salts of the alkaloids are also precipitated by tannin. Alkaline solutions of tannin become rapidly brown when exposed to air.

According to Dr. Strecker tannin is a glucoside, which under various influences is split up into gallic acid and glucose, the formula of tannin being $C_{27}H_{24}O_{17}$; its splitting up into glucose is exhibited by—

 $C_{27}H_{22}O_{17} + 4H_2O = \underbrace{3(C_7H_6O_5)}_{Gallic \ acid.} + \underbrace{C_6H_{12}O_6}_{Sugar.}$

This reaction takes place—(1) under the influence of a ferment, when coarsely pulverised and moistened nut-galls are left to become mouldy, or also when the decoctions are kept for a length of time; (2) by boiling tannin with very dilute sulphuric acid, or with a dilute caustic alkaline solution.

Gallic acid is always present to some extent in galls, and in the other astringent substances above enumerated. It can be artificially obtained by decomposing di-iodosalycilic acid by means of caustic potassa. Gallic acid forms silky acicular crystals, soluble in 100 parts of cold and in 3 of warm water, and also in alcohol and ether: its formula is $C_7H_6O_5H_2O$.

When submitted to a temperature of about 210° it is decomposed, yielding carbonic and pyrogallic acids; at a higher temperature water, carbonic acid, and gallohumic acid are formed.

Gallic acid is dissolved by concentrated sulphuric acid; but since the gallic acid is hereby deprived of its water of constitution, it is simultaneously converted into rufigallic acid, $C_7H_4O_4$.

Pyrogallic acid sublimes in white scaly crystals, and is chiefly remarkable for its rapid absorption of oxygen when in alkaline solution, being thereby converted into substances belonging to the ulmic series.

Since the goodness of galls and other astringent materials depends on the quantity of tannin they contain, it is of importance to have a method of rapidly estimating that quantity. M. Fehling has proposed, for this purpose, the application of a standard solution of gelatin containing 10 grms. to the litre: a proof test is made, in order thereby to estimate with precision the weight of the tannin which is precipitated by 1 c.c. of this liquid. The wares are tested by exhausting 1 grm. with pure distilled water, and from the bulk of gelatin solution employed the quantity of tannin is calculated: the tannin solution should be slightly acidulated or mixed with a little alum, since this promotes the rapid precipitation of the tanno-gelatin compound; instead of gelatine solution, a solution of tartar emetic or of sulphate of cinchonin can be employed.

Dr. Günther, of St. Petersburg, has recently investigated the different analytical methods in use for the determination of the quantity of tannic acid present in galls, catechu, ratanhia, kino, and other drugs. In an exhaustive treatise* are described the various methods which have been practically tested by the author with great care; as a general result arrived at by him, we may state here that none of the different methods answer the purpose completely, that is to say, that a method which yields excellent results with nutgalls is not equally suitable for sumac, catechu, &c.; for the good reason, that these materials contain either other substances along with tannic acid or specific modifications of the same.

M. Mittenzwei proposes to estimate the tannin in nut-galls by determining the volume of oxygen absorbed in the presence of an alkali:—I grm. of tannin absorbs 175 c.c. of oxygen; gallic acid is thus formed, o'7 grm. of which absorbs also 175 c.c. of oxygen; since galls contain, as above stated, both gallic and tannic acids, the total absorption of oxygen by these together is first determined, and that of the gallic acid present is next estimated in a fresh portion of the galls after the tannic acid has been removed therefrom by a piece of skin. For commercial purposes this method is utterly out of the question.

Löwenthal oxidises the tannin by means of permanganate of potash or bleaching lime in standard solution, an excess of sulphate of indigo being added. The tannin and indigo are oxidised simultaneously, and with the disappearance of the colour the operation is completed. The articles required for the process are a standard solution of pure tannin, containing in 1 c.c. o'oor grm. of tannin dried at 212° F.; a dilute solution of the best extract of indigo, containing about 30 grms. of the paste per litre; and a clear solution of chloride of lime, which must be preserved in a dark place. The first step is to standardise the solutions. To this end 20 c.c. of the indigo-

^{* &}quot;Pharmaceutische Zeitschrift für Russland," No. 6 and following, 1870.

liquid are put in a beaker with 1000 c.c. of water and 10 of hydrochloric (muriatic) acid. The beaker is then set in a white porcelain basin, or a soup-plate, and the chloride of lime liquor is carefully added, with constant stirring, till the green colour disappears, and is replaced by a faint yellow. The quantity of chloride of lime solution required to produce this result is then read off and noted. A fresh quantity of the indigo solution is then mixed with hydrochloric acid water exactly as above: 20 c.c. of the solution of tannin are then added, and the chloride of lime liquor is dropped in as before till the green tint finally disappears. From the number of degrees of the chloride of lime solution required to produce this effect we subtract the number found as above for the indigo solution alone. The remainder is the amount of the chloride of lime solution, representing 0.020 grm. of tannin. It is advisable that about 100 c.c. of the chloride of lime liquor may correspond to o'2 grm. of tannin. In determining the value of a sample of sumac, myrobalans, &c., we take 5 grms., suitably ground up; boil it for thirty to forty-five minutes with } litre of pure water, let it cool, transfer the whole to a litre flask, make up with water to the exact bulk of I litre, and shake up. When it has settled, 30 c.c. of the clear liquid are taken out with a pipette for the actual analysis. This quantity is mixed with the indigo solution, water, and hydrochloric acid as above, and the standard chloride of lime-liquor is then dropped in from the burette till the green colour disappears. If this process is carefully performed the results are slightly too high.

Hammer takes the specific gravity of a solution of tannin, removes the tannin, and takes the specific gravity again. From the loss apparent on this second determination the amount of tannin present is calculated by means of

the accompanying table. (See next page).

The specific gravity of the solution to be tested is taken either with an ordinary specific gravity bottle or a very fine hydrometer. For withdrawing the tannin from its solutions the material used is raw hide. A piece of this, cleaned and prepared as if for tanning, is well washed, dried at a gentle heat till its weight becomes constant, rasped to powder, and preserved in that state in a well-stoppered bottle. When wanted for the performance of an analysis an amount of this, not less than four times the supposed quantity of tannin, is weighed out, softened by steeping in water, well squeezed in a fine linen cloth, so as to remove any superfluous moisture which would otherwise dilute the solution, and then digested for a short time in the liquid to be tested, with frequent shaking. In this manner the whole of the tannin may be withdrawn from a liquid. In using this method the sumac, galls, &c., must first be powdered, rasped, or otherwise well divided, boiled with water, and exhausted in a displacement-apparatus. I part of the substance should be completely extracted with 10 to 12 parts of water. The extract is made up with water to some known weight, well shaken up to secure homogeneous mixture, and the specific gravity of the liquid ascertained. A portion of the solution, rather more than sufficient for the determination of the specific gravity, is weighed off, and digested with an excess of hide-raspings, with frequent agitation, as explained above. The liquid is then filtered through fine linen into a hydrometer-tube or specific-gravity bottle, and its specific gravity determined once more. From the loss the amount of tannin may be calculated.

Sp. gr. at 15' C59' F.			Tannin er cent.	Sp. gr. at 15° C.=59° F.			Tannin per cent.
1,0000	 		 0.0	1.0104	 	 	2.6
1.0004	 	6 0	 O.I	1.0108	 	 	2.7
1.0008	 		 0°2	1.0113	 	 	2.8
1'0012	 		 0.3	1.0119	 	 	2.9
1.0019	 		 0'4	1.0150	 	 	3.0
1.0050	 		 0.2	1.0154	 	 	3.1
1.0024	 		 0.9	1.0138	 	 	3.5
1,0058	 		 0.2	1.0135	 	 	3.3
1.0033	 		 0.8	1.0136	 	 	3.4
1.0036	 		 0.0	1.0140	 	 	3.2
1.0040	 		 I.O	1.0144	 	 	3.6
1.0044	 		 I.I	1.0148	 	 	3.7
1.0048	 		 1.2	1.0125	 	 	3.8
1'0052	 		 1.3	1.0126	 	 	3.9
1.0026	 		 1.4	1.0160	 	 	4.0
1,0000	 		 r.2	1.0164	 	 	4°I
1.0064	 		 1.6	1.0168	 	 	4'2
1.0098	 		 1.7	1.012	 	 	4'3
1'0072	 		 1.8	1.0176	 	 	4.4
1.0076	 		 1,0	1.0180	 	 	4.2
1,0080	 		 2.0	1.0184	 	 	4.6
1.0084	 		 2°I	1,0188	 	 	4.7
1,0088	 		 2.5	1.0193	 	 	4.8
1.0003	 		 2.3	1.0100	 	 	4.9
1.0006	 - +		 2.4	1.0501	 	 	5.0
1.0100	 		 2.2				

Persoz prepares a standard solution of tannin, containing 10 grms. per litre, and another solution of 8 grms. tin crystals and 2 grms. sal-ammoniac in 1 litre of water. A number of glass cylinders are provided, graduated in cubic centimetres, and holding each 200 c.c. To perform an analysis he puts into two cylinders 100 c.c. of the tin liquid each. To the first he adds then 100 c.c. of the standard tannin solution, and to the second 100 c.c. of the extract of 1 grm. of the sample of astringent material under examination. Both cylinders are then, after well stirring up, set aside for twelve hours, when the volumes of the precipitates are read by the graduation on the glass, and the amount of tannin per cent is thus calculated.

Risler-Beunat collects the precipitate formed on adding the tin solution to the extract of an astringent, filters, washes, dries at 212° F., and weighs. The residue is then ignited and peroxidised by aid of nitrate of ammonia. The peroxide of tin thus obtained is weighed, the amount of protoxide which it represents is found by calculation, and this being deducted from the first found weight the remainder is tannin.

According to Dr. Stenhouse, the tannic acid present in valonia does not yield, on being boiled with dilute sulphuric acid, gallic acid and sugar, but, instead of the former, a reddish-brown substance, which is sparingly soluble in alcohol. The tannin of divi-divi also differs from that of galls, as is also the case with the astringent principle of myrobalans, while sumac contains

chiefly gallo-tannic as well as gallic acids. There is a great field for research open as regards the native tannic and gallic acid compounds and substances allied thereto, which, in many respects, are only very imperfectly known.

We have now to explain the use of these substances in dyeing and printing. Nutgalls are used for the preparation of tannin, for the manufacture of Morocco leather, for the preparation of black writing-ink of good quality, and next in many dyeing operations. Tannin (tannic acid) prepared as above described is applied in some instances for fixing certain colouring matters, especially the aniline derivatives, acting as a mordant. The galls known as Knoppern or Piedmont galls are little used in England, though abroad they are employed for tanning skins for the purpose of Morocco leather, and also in dyeing and printing, while an extract of these galls is made for the latter purpose. Valonias are often employed on the Continent instead of nutgalls, but in this country, except in some operations of silk dyeing, they are not extensively used in dyeing and printing. The tanners, however, use them largely, and with decided advantage. Sumac is also substituted for galls, and is, although less rich in tannic acid, advantageous in some cases, on account of the pure colours it yields. All the astringent matters above named, especially sumac, behave as if they contained a yellow colouring matter, imparting a more or less yellowish-drab shade to all fibres, cotton, wool, and silk, but less readily to flax and hemp if mordanted with alumina. The colour imparted under that condition by sumac is decidedly yellow, but that given by nutgalls is a greyish-drab: if the temperature of the dye-bath be raised, or the tissue immediately after dyeing exposed to air, the colour becomes dirty, like iron rust.

Cotton which has been impregnated with oil (see Turkey-red) becomes, when placed in a sumac bath, pale yellow, and turns, on subsequent mordanting, to bright yellow; with acetate of tin as a mordant sumac yields a yellow, and with zinc salts a brown upon cotton. Analogous shades can be prepared by first steeping the cotton in the sumac decoction, and aluming the

tissues afterwards, but the depth of shade is less.

With the per-salts of iron as a mordant, the astringent materials yield, according to the strength of the mordant, grey, blackish grey, or bluish grey tints. The chief use made of sumac consists, as far as its application in dyeing and printing is concerned, in being employed, with salts of iron and copper, as mordants and oxidising agents, sometimes along with logwood, for the production of greys and blacks. Nutgalls and sumac are used in Turkeyred dyeing, as we have explained while treating of that process. When it is desired to convert the greys and olives produced by quercitron into chocolate or cinnamon-brown by means of the subsequent application of madder, it is necessary to add to the madder bath an astringent decoction in order to prevent the decomposition of the quercitron colour by the madder bath; sumac is also applied sometimes to the dunging mixture. (See Madder, &c.) Stannated tissues (mordanted with tin compounds) destined to be dyed with corallin and other coal-tar colours, are frequently passed through decoctions of galls or myrobalans, in order to obtain the proper precipitation and fixing of these colours upon the tissues, chiefly cotton. Calico mordanted with pyrolignite of iron, fixed by ageing and passing through a solution of an alkaline silicate, is dyed grey by means of sumac, galls, myrobalans, bablah, &c., each of which substances taken separately only

serves for the production of that shade of colour. The grey obtained by the use of Sicilian sumac is somewhat reddish, and this the more so the higher the temperature of the decoction while applied; it is therefore necessary not to increase the heat above 50°, and to steep the goods only for about half-an-hour. The shade of grey produced by galls is more ashy, while that produced by bablah holds an intermediate position between the two.

The French sumac is less liable to yield foxy greys and blacks by being exposed to a too high temperature. Nutgalls are rarely employed for dyeing printed goods, on account of the property of galls of injuring the iron mordants, that is to say, dissolving them, and spoiling the pattern by making it spotted; a small quantity of galls added to logwood for black dyeing turns the shade bluish-black. Bablah yields greys as pure as galls, while the colour is brighter than that yielded by sumac, and it moreover soils the white portions of the patterns less. Valonia holds the middle place between galls and bablah as regards the colours it produces, but it is most advantageously employed along with logwood; when it is desired to dye calico, silk, or wool uniformly black, astringent matters are very generally mixed with logwood. For cotton, for instance, the operation is begun with a steeping of the tissue for 12 hours in a bath of myrobalans, sumac, or galls, the goods being placed therein while hot, and left until the liquid is quite cold; the pieces are next passed through lime-water (weak milk of lime), then put in a bath of sulphate of copper, after that in a boiling logwood decoction, and next again in a solution containing sulphates of iron and copper mixed. Sometimes the operation is performed by first mordanting the goods with a salt of iron, and dyeing in a bath made up of decoctions of galls, logwood, and sumac mixed. Woollen goods, broadcloth chiefly, are dyed black by first dyeing them indigoblue (vat blue), and after that the tissue is placed in a boiling bath made up of myrobalans and logwood (so called Sédan black), or in a boiling bath of sumac, logwood, and fustic (so called Elbeuf black); afterwards, there is added to these baths, while the goods are yet steeped therein, either sulphate of iron alone, or a mixture of sulphate of iron and sulphate of copper, or, in place of these, bichromate of potash. Silk is dyed black by being alternately steeped in astringent baths and a solution of pyrolignite of iron.

Decoctions of galls, sumac, and valonia are ingredients in some kinds of steam-grey and application-grey for cotton, along with acetate or pyrolignite of iron; the same astringent decoctions, mixed with logwood extract and red liquor, or an iron mordant accompanied by an oxidising material, i.e., a coppersalt and sal-ammoniac, are applied for the production upon cotton and wool of so-called wood, wainscot, and other complex colours. The astringent decoctions are also used, along with logwood extract, for the production upon silk of some steam-blacks, nitro-sulphate of iron being used as a mordant.

Our ordinary black writing-ink is a ready-made colour which, by its mode of preparation, is capable of fixing itself on paper. The best ink is made by adding to a decoction of Aleppo, or Chinese galls, a solution of proto-sulphate of iron, in which case the precipitation of the tanno-gallate of iron is rendered so slow as to make it appear as if the ink were a solution, which, however, it is not; and the addition of some gum and sugar is required to keep the precipitate suspended. One of the great drawbacks of ink thus prepared is its becoming readily mouldy and viscous. The former defect is best remedied by the

addition to the ink of some corrosive sublimate, or, if this poison is dreaded, there may be added a few drops of essential oil of cloves or a trace of carbolic acid. The viscosity of ink is frequently due to the use of inferior materials in its preparation, and to the neglect of filtering it through good filtering-paper, an operation which is always very tedious.

Gallein.

A dye, or rather class of dyes, may here be noticed which stand in a close relation to the astringents, and are prepared from pyrogallic acid. The first step is the preparation of gallein. For this end, the inventor, Baeyer, heats a mixture of 1 part of anhydrous phthalic acid and 2 parts of pyrogallic acid to 200° C., and keeps the mass at that temperature for some hours. When cold, the residue is treated with hot alcohol, the solution is filtered and diluted with water, which throws down a precipitate of the new body, gallein. It is of a reddish-brown colour, but when in large lumps it exhibits a greenish-yellow metallic reflection. It is insoluble in cold, and sparingly soluble in boiling, water, forming a red solution. In alcohol, it dissolves readily with a deep red colour. It is also soluble in caustic potash lye with a blue, and in ammonia with a violet, colour.

Gallein is in many respects analogous to hæmatin. Trimesic, pyromellitic and prehnitic acids, and the oil of bitter almonds also yield gallein on fusion with pyrogallic acid.

The composition of gallein is found to be $C_{18}H_{14}O_7$. If treated with zinc and dilute sulphuric acid, it is converted into gallin,—a solid, colourless, crystalline body, soluble in ether, and still more readily in an aqueous solution of pyrogallic acid. When dried in a vacuum, its composition was found to correspond with the formula $C_{18}H_{16}O_6$. It is sparingly soluble in cold, but readily in boiling water, and still more readily in alcohol. Both in the solid state and in solution it becomes very readily pink-coloured. It dyes tissues in the same manner as gallein.

Gallein, if treated with concentrated sulphuric acid at 200° C., yields cœrulein, $C_{18}H_{10}O_6$. This body is almost insoluble in water, alcohol, and ether. In acetic acid it dissolves more readily, forming a dirty green solution. It is easily soluble in hot aniline, yielding a solution of a splendid deep blue colour, which, if acidified with acetic acid, dyes wool indigo-blue. Cœrulein dissolves in alkaline liquids with a beautiful green colour. The solution dyes tissues previously mordanted with alumina a fine green. If an iron mordant be used, the resulting shades are brown. Both these dyes are fast, and resist soaping. There appears to be a resemblance between cœrulein and Lo-kao (Chinese green).

Reducing agents convert cœrulein into cœrulin, which dissolves in ether with a yellow colour. If anhydrous phthalic acid is allowed to act upon resorcin, fluorescein is formed,—a yellowish-red body soluble in alcohol. It is a substantive colour, and dyes silk and wool yellow without the aid of any mordant.

The following substances, though possessing tinctorial powers, and capable of being applied in dyeing and printing, are, from a variety of reasons, not in actual use:—

Alder Bark contains a colouring principle, along with tannin. With

preparations of tin and alumina, it yields a variety of buffs, yellowish-brown and orange shades, which have no distinctive recommendation. In some parts of England, it was formerly used for dyeing blacks on silks. The bark was well boiled up in soft water, and the mixture was allowed to act upon scrap iron for a considerable time. The blacks dyed with this liquid are said to have been remarkably rich, soft, and permanent. It was also employed, like logwood and galls, with copperas and iron-liquor, and was used alone with fustic for browns. It is still, we believe, used by jobbing dyers in rural districts.

Algaroba, a substance not unlike catechu in appearance and properties. It is obtained from the La Plata, and contains tannin, mixed with a deep brown colouring matter.

Amalic Acid.—This substance is obtained by decomposing caffein by means of chlorine gas. Its composition is $C_4(CH_3)_4N_4O_7+H_2O$. It forms transparent colourless crystals which do not lose their water at 100° C. With ammonia, potash, soda, and baryta, it forms a series of compounds of a fine violet. The scarcity of the material prevents these from being of any practical importance.

Anthokirrin.—A yellow colouring matter obtained from the flowers of the toad-flax (Antirrhinum linaria). The flowers are extracted with hot alcohol, the liquid evaporated to dryness, and the dry residue exhausted with water to remove sugar and gum. The insoluble part is then treated with alcohol, the solution is filtered and evaporated to dryness, and the residue taken up with ether. On evaporating the ethereal solution, the colouring matter is deposited in yellow needles, which, if dried and exposed to heat, sublime undecomposed. Alkaline liquids dissolve anthokirrin with a red colour. In ammonia and alkaline carbonates it dissolves with a yellow colour, and is re-precipitated by acids. Concentrated mineral acids dissolve it with a red colour, which turns to a yellow on standing. Strong aqueous solutions give an orange precipitate with the acetate of lead, a yellowish-green with salts of copper, and an orange with solutions of tin. With alum it gives a yellow lake. It dyes yellow shades of little value.

Areca Nuts have been employed, or at least recommended as an astringent. They contain also areca-red, a brownish-red dye, insoluble in cold but soluble in boiling water. ("Morin. Journ. Pharm.," viii., 449).

Bablah, Neb-Neb, Neb-Nab, or Babulah is the fruit of Mimosa cineraria, a tree growing in India and along the Senegal. It contains gallic and tannic acids—the former in considerable amount—and a red colouring matter. The total amount of tannin and gallic acid in African samples is, according to Chevreul, 57 per cent, and in those from India 49 per cent. It cannot be used as a substitute for sumac, galls, or myrobalans on account of the accompanying red matter, except in some particular cases. With mordants of iron and alumina it yields fawn and drab shades. Its reputed power of rendering all colours fast is imaginary, and it is now very rarely used.

Barbatimas.—An astringent, from Brazil.

Bearberry, the fruit of Arbutus Uva-Ursi, contains astringent matter, and is sometimes used in dyeing black.

Bilberries (Whinberries or Whortleberries), the fruit of *Vaccinium myrtillus*, were formerly employed for producing certain blue and purple shades on silk. The colours thus obtained are very fugitive.

Brauna-wood (Melanoxylon brauna) is furnished by a tree growing in the province of Minas Geraes, in Brazil. Its use was patented in 1857, and it was said to have a strong affinity for cotton "with or without mordants," and to produce browns, drabs, slates, salmons, buffs, fawns, and blacks more permanent than those obtained by other means.

Butter-nut Bark, the bark of Juglans alba, a kind of walnut, growing in the north-eastern states of the American Union. It is said to yield fast blacks with iron mordants, and deep browns with preparations of alumina.

Cactin, a red colouring matter obtained from the flowers of many species of cactus, especially *C. speciosus*. It has been examined by Vogel and Wittstein, and is theoretically interesting on account of its relations to cochineal. It has been suggested that the cochineal insect does not actually generate the colouring matter which it contains, but merely extracts and concentrates principles pre-existent in the juices of the plant upon which it feeds, and which is also developed, without its aid, in the flowers. So far, this view does not seem borne out by experiment. A considerable quantity of a carmine-red colouring matter can be extracted from the cactus flowers by treatment with weak alcohol. It is soluble in water. From the portion left undissolved by the dilute alcohol, a further amount of a scarlet colour is obtained by treatment with a mixture of alcohol and ether. Neither of these colours is in use, and a further examination of their properties is needed. The fruit of the *C. cochenilifer* contains also a coloured juice, which imparts a deep red tinge to the urine of animals fed upon it.

Canadian Yellow-root.—The root of Hydrastis Canadensis affords a yellow dye—hydrastin, which is turned red by sulphuric acid and chromate of potash.

Carapa-root.—The root of a plant found in Guayana. Its bark contains one yellow and two red colouring principles. (See "Journal de Pharmacie," xxxv., p. 189.

Chestnut.—The whole tree, especially the nuts and the sap, contains astringent matter, which was patented by C. L. Girourd as a substitute for gall-nuts, under the horrible name of "damajavag." The extract of chestnut is still occasionally used on the Continent for adulterating the extracts of logwood and other dye-woods.

Chicory.—The leaves of this plant are used, according to D. Metcalf's patent, as a substitute for woad in the indigo-vat. Like the leaves of rhubarb when applied to the same purpose, they probably serve merely to promote fermentation.

Chrysoretin .- A yellow, resinous matter, obtained from senna leaves.

Coccedia viridis.—This plant yields, according to Salm Horstmar, a green dye, distinct from chlorophyll. ("Pogg. Ann.," xciv., p. 466, and cxv., p. 176).

Cocoa-nut Tree.—In a patent, obtained by Mr. J. H. Baker (No. 5139, March 29, 1825), the whole or every part of this tree is claimed as a dyeware, especially the husk enclosing the fruit, and the foot-stalks of the leaves. The dye was to be extracted by water, cold or boiling, or by solutions of lime, potash, ammonia, &c., and was to serve for dyeing nankeens, blue-blacks, &c. The infusion was likewise to serve as a substitute for nut-galls in Turkey-red dyeing. The material does not appear ever to have come into practical use.

Cork.—According to T. Bury's patent (Feb. 18, 1823), the bark of the cork-tree may be used in dyeing nankeens upon cotton, along with the

"usual mordant." Cork-cutters' waste, digested with nitric acid, yields a primrose-yellow colouring matter,—probably an impure or modified picric acid,—which was at one time used for dyeing yellow waistcoatings.

Dyer's Woodruf (Asperula tinctoria) is cultivated and used to a small extent in Dalmatia as a substitute for madder.

Gammam.—A dye-ware from Tunis. Samples were sent to the Exhibition of 1851, but it has not been introduced into the market.

Golden Rod (Solidago Canadensis) is stated to produce good yellow shades,—similar to those yielded by weld,—both upon animal and vegetable tissues. It is not met with in the English market. Its mordant is alum.

Green Ebony.—A wood sold under this name has sometimes been used as a yellow dye, especially in compound colours, such as greens.

Heath.—In former times common heath was used as a dye-ware, and gave a yellow colour upon woollen goods. It is now quite superseded by richer woods and barks.

Hellebore (Helleborus trifolius).—The Canadian three-leaved hellebore is used by the native Indians for dyeing skins and wool a yellow.

Hemlock.—The bark of the "hemlock spruce" (Abies Americana) contains tannin, and has been experimentally used for dyeing. The results were not encouraging, as the blacks and other sad colours produced have an unpleasant rusty-red, or, as it is technically called, "foxy" reflection.

Hiccory.—The bark and nuts of the "American hiccory, or walnut tree" were claimed by Dr. Bancroft, in his patent of October 23, 1775, as capable of producing yellow and green colours with a mordant of alum and verdigris. The material never came into extended use.

Holly.—Ilixanthine, a principle obtained from the common holly, is insoluble in cold water, soluble in hot water and alcohol, with a yellow colour; insoluble in ether, but soluble in hot concentrated hydrochloric acid. With alum it dyes a yellow, and with ferric chlorides a green.

Hollyhock.—The common garden hollyhock is said to contain, in its stem, a blue colouring matter not unlike indigo. This colour has never been obtained upon a manufacturing scale, and its properties are still a matter of dispute.

Horse-chestnut.—The cotyledons of the horse-chestnut fruits contain, according to Rochleder, argyrescin, a yellow colouring matter.

Horse-radish.—This plant contains a yellow colouring principle, not in use.

Khail-cedra, obtained from Khaya Senegalensis, yields red or yellow colours. (Caventon, "Journ. Pharm.," xvi., 355, and xxxiii., 123).

Lamium album (The Dead Nettle).—This plant yields yellow and green colours of no value.

Lamium purpureum produces, with preparations of tin, a reddish-grey, and with iron liquor a greenish colour.

Lawsonia inermis, the henna of the Arabs, is used in the East for staining horse-hair, leather, and human finger-nails a reddish-purple. Its use has been patented in France for dyeing blacks.

Lithospermum arvense.—The root-bark yields a red colour resembling that obtained from alkanet root. It forms, however, a blue solution in ether, whilst alkanet gives with the same solvent a red.

Mahaleb.—A shrub whose fruit yields a violet dye.

Mahogany-tree Bark.—This bark contains a small amount of colouring matter, and has been used for producing a variety of sad shades. The result was unsatisfactory, and the ware is not in use in England.

Mangrove.—The bark of the red mangrove was patented by Dr. Bancroft as yielding a variety of red, brown, and nankeen shades, with alum, copper, lead, &c. It was at one time in common use, but has been altogether abandoned.

Nitrocuminic Acid.—Jules Persoz states that this acid, when hot, communicates to calico a variety of shades from scarlet to pink.

Nucin.—Green walnut-shells are extracted with ether. The extract is treated with neutral sulphate of copper till it assumes a blood-red colour. It is now filtered, and mixed with nitric acid till it turns to a greenish-blue. The nucin thus set free is dissolved in ether, and evaporated over sulphuric acid. It is a yellow powder, which dissolves in ammonia with a red colour.

Nymphæa alba (The White Water-Lily), described in some works under the name nenuphar, contains astringent matter, and is sometimes used in

Eastern Europe as a substitute for galls or sumac.

Palisander Wood is a red dye-wood obtained from Madagascar. It resembles santal-wood in many of its properties, but it produces shades less orange in their tone. It must be observed that the names Palisander and Palisandre are, on the Continent, often applied to the common rosewood of cabinet-makers. (See Arnaudon, "Ciment.," viii., p. 278).

Paracarthamin is obtained by the action of sodium amalgam upon rutin. It is turned green by alkalies, and red by acids. It is found in dogwood, the blackberry, the willow-stem, and in the bark of certain acacias.

Phycocyan, Phycoerythrin, Phycohæmatin, are blue and red colours obtained by Kützing from sea-weed (Bytiplea tinctoria). The colours are

quickly destroyed by sunlight.

Pittacal.—On adding baryta-water to solution of picamar (tar-oil deprived of its acid), pittacal falls down as a dark-blue powder, inodorous, non-volatile, very sparingly soluble in water. It dissolves in sulphuric acid with a green colour, having a crimson cast. With tin and alum mordants, it dyes fast blues on cotton.

Polygonum tinctorium.—The fresh leaves are exhausted with ether, and a portion of the liquid is distilled off, when some indigo-blue is separated. The remainder is evaporated to dryness, and exhausted with alcohol. The extract is filtered, evaporated again to dryness, and the residue exhausted with hot water. A hard reddish mass remains, insoluble in water, slightly soluble in alkaline liquids and in acetic acid, and readily soluble in ether. The alcoholic solution forms a fine red lake with alum.

Pomegranate Root Bark.—This bark yields shades similar to those obtained from quercitron bark.

Purple Heart.—The wood of *Copiaba pubifolia*, a tree of Guayana. It produces purple shades with tin and alum mordants.

Privet Berries contain ligulin, a crimson dye, soluble in water and alcohol, but insoluble in ether. Privet leaves contain ligustrin, insoluble in ether and alcohol, but soluble in water and dilute alcohol. Sulphuric acid turns the solution a deep indigo-blue, which, when diluted with water, becomes violet. These solutions are not precipitated by metallic salts.

Saw-wort (Serratula tinctoria).—This plant is stated by Bancroft to yield yellow shades resembling those produced by weld.

Sunflower Seeds contain helianthic acid, which, when treated with dilute hydrochloric acid in a current of hydrogen, is resolved into glucose and a violet dye.

"Syria."—Under this curious name is sold the imperfectly-exhausted residue of Coccus ilicis.

Viridic Acid, a colouring matter contained in unroasted coffee. It is turned a fine deep green by alkalies, and dissolves in sulphuric acid with a crimson colour, but on the addition of water is deposited in blue flakes. White of egg placed in contact with raw coffee-beans takes a fine green colour which might be advantageously used by confectioners, instead of the unwhole-some pigments sometimes employed.

Virginia Creeper (Ampelopsis hederacea).—The red leaves of this well-known climber contain a red colouring matter, cissotannic acid.

Preparation of Extracts of Dye-Woods.

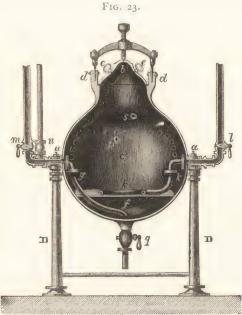
We have now to turn our attention to a collateral branch of the dyeing operations, viz., the mode of preparation of extracts of the dye-woods employed by the dyers and calico-printers. This manufacture has sprung up with the more extensive use of the wares in question, and is of comparatively recent date, owing in part also its origin to the fact that the dye-woods are not directly fit for use in the calico-printing business. The manufacture of these extracts is carried to a high degree of perfection, and is performed in the following manner:—By means of suitable machinery, the woods are reduced to a coarse powder, or to small chips cut generally in a direction perpendicular to their fibres. This operation requires also a large amount of moving power. The coarse powder or chips thus obtained are directly exhausted by means of water, or are left exposed in heaps, in a moist state, to a kind of oxidising fermentation, whereby the solubility of the colouring matter is increased and the exhaustion thereof by water facilitated. This is especially done for logwood.

It is clear that in order to carry on the exhaustion of the woods with the least possible expenditure the quantity of water to be used should be as small as possible, because the greater part of that vehicle has to be got rid of by evaporation. Some manufacturers carry on their operations in open tanks, applying water at 60° or 100°, but others prefer to work at a temperature above 100°, and then of course in closed vessels. The annexed figure (Fig. 23) gives a view of the construction of these vessels: c represents a copper boiler fixed between two cast-iron columns, p, so as to be movable on the imaginary axis, a a, that is to say that c at the top of the figure can, by turning the boiler round that axis, be brought to where q stands in the figure, and be reversed again if required; b, manhole, hermetically closed by means of the screw, c; e e, two handles or rings, fit for lifting off the piece b, manhole cover; f, coppermade false bottom, perforated with holes; to this piece of copper is fastened a piece of brass wire gauze of narrow gauge; k, perforated worm tube, which by means of the pipe, l, communicates with a steam-boiler. The pipe g, which communicates with the cavity below the false bottom, is in connection with three tubes, furnished with three taps, m, n, and o (the latter is not,

however, visible in the cut, being placed in front of and before n); m serves for the introduction of pure water, n and o for running off the decoction made of the dye-wood under pressure of the steam, but if the steam is turned off the liquor is run off by q, a small air admission tap being provided at p.

The evaporation of the liquors obtained from the exhaustion of the woods with water is effected in various ways; sometimes vacuum-pans are used, but they do not answer the purpose very well for extracts which have to be concentrated above a specific gravity of 1.134, on account chiefly of the difficulty experienced by the bubbles of aqueous vapour in escaping from a mass of viscous liquid; the evaporation is therefore most frequently carried on by means of double bottomed shallow pans heated by steam.

In order to make extract of quercitron, this material, which is imported ready pulverised, has to be boiled for a length of time with water, and the



liquid to be separated from the dregs by filtration, the residue being pressed,

and the clear liquid is then evaporated to dryness.

The extracts of dye-woods contain, in addition to the colouring matter, all the soluble salts contained in the wood, also the nitrogenous matter, the glucosides, and other vegetable matters soluble in water, which it would be very useful to remove if it could be done efficiently and without too great expense, since most of these substances impair the beauty and brightness of the dyes made with these extracts, and, moreover, add to the cost of transport, as well as render the extract liable to become mouldy. A great desideratum also is the obtaining of inexpensive and suitable solvents for the removal of the colouring matters from the woods in a purer state. It has been proposed

to extract the colouring matters of dye-woods by means of weak solutions of soda, potash, or ammonia, caustic or carbonated, and to neutralise the decoction thus obtained by the cautious addition of an acid. Others have reversed the method, treating the dye-ware first with an acid or an acid salt, and then neutralising with an alkali. Processes of this nature have been patented by Leeshing, No. 1160 (1855), and by Roberts and Dale, No. 1988 (1857). The objection to operations of this nature is, that even brief contact with alkaline liquids, especially at an elevated temperature, impairs the beauty of most of the colouring matters concerned. The utilisation of the exhausted wood also is a matter of importance; an attempt has been made to manufacture acetic acid from the residues, but this requires complicated apparatus; perhaps the utilisation of this material along with other substances, as compressed artificial fuel, might be worth while trying.

CHAPTER VII.

MORDANTS.

THOUGH much has been said, incidentally, in the preceding pages concerning mordants, their systematic consideration remains to be undertaken. The subject is remarkably complicated from two reasons:—Different dyers and printers produce identical results by means so widely varying, that what one finds in his peculiar mode of procedure to be useful or even necessary, another would at once put aside as worthless. Again, the nomenclature of all the articles used in tinctorial industry is in the highest degree perplexing. One and the same substance is known under different names, some of them originating in the workshop; others being specimens of almost every stage through which chemical theory has passed. As far as possible we shall endeavour to point out which of these substances are identical, and which really distinct.

A few general considerations will be necessary before entering upon the practical part of the subject. That mordants are a class of bodies which serve to fix colouring bodies upon textile fibres is well known. It will have been perceived from the foregoing portion of this work that few colouring matters are able to attach themselves to cellulose—whether in the form of cotton, linen, or jute, &c.—without the interposition of some third body, which having an affinity for both, brings them into a more or less permanent state of combination. Animal tissues and fibres, wool, alpaca, hair, horn, leather, and silk combine unaided with a much larger number of dyes. Yet even in their case mordants are often employed to give additional brightness and permanence to the shades produced, or to modify the effect in some peculiar manner. Hence most mordants are at the same time alterants, the shade fixed upon the fibre being not that of the dye-ware in its free state, but that of a combination formed between some one or more of its constituents and the mordant.

A mordant to be useful must possess a peculiar combination of qualities. It must have a strong affinity or attraction at once for the fibre and the colour. But these attractions must not pass certain easily recognised limits. If too powerful, the work done will be uneven and spotty; certain parts of the goods either from first entering the dye-pan, from presenting a slightly abraded surface,* or from a variety of other causes, will take up an excess of the colour,

^{*} The mechanical condition of the surface of a tissue has a powerfully modifying effect upon its affinity for mordants and colours. Any portion which has been roughened by friction takes a deeper, though often a duller, colour than parts of the same fabric which remain smooth and

whilst the remaining parts receive less. If, on the other hand, the affinity of the mordant for fibre and colour is too feeble in itself, or is over-balanced by some other body present, the shades resulting will be impoverished, meagre, and probably fugitive.

If a mordant, as is sometimes the case, has a much more decided affinity for the colouring matter than for the cloth or yarn, the colour produced is deposited not on or in the fibre, but at the bottom of the dye-beck, in the shape of a lake or pigment, whilst the goods are merely stained or smeared with colour. Hence, not every metallic base or salt which has a strong affinity for colouring matters, and forms abundant and possibly beautiful precipitates in solutions of dye-wares, is fitted for use as a mordant. It is necessary for the mordant to combine both with fibre and colour with regularity, and not too rapidly, so that the compound formed may not be loosely plastered over the surface of the fibre, but may inter-penetrate its substance. The result will, otherwise, be uneven, fugitive, and dull.

Another essential condition is that the mordant must have no injurious effect upon the fibre. If too strongly acid or alkaline it will have a corrosive action, and the goods, as it is technically called, will be "tendered." The colouring matter may also be "flattened" or deprived of its lustre by an ill-compounded mordant. The great majority of mordants are acid, and the practical difficulty is duly to proportion the acid to the base, so as to produce a well-balanced whole. If there is too little acid the mordant becomes too "dead," and the base is delivered to the fibre rapidly and irregularly. If the acid is in excess the mordant parts with its base too sparingly and slowly, and the tissue is weakened.

It is also important that mordants should not of themselves affect the colour of the fibre. When, like the salts of iron, manganese, or copper, they possess an independent tinctorial power, their use is limited to some particular set of shades. Thus, an iron mordant imparts of itself a buff colour to vegetable fibre. It can, therefore, generally be used only where the shade intended is a black, brown, olive, drab, or some other "sad" colour. Compounds of tin and of alumina, which leave the fibre colourless, can be used for light and bright shades.

Mordants, as a matter of course, are presented to the fibre and to the colour in a liquid state, but they must be capable of becoming insoluble as the combination is accomplished. This change of condition, from a soluble to an insoluble state, is brought about in several ways. Frequently it is a case

glossy. This is a serious difficulty for the jobbing dyer, since garments which have been worn always present inequalities of surface, and are, therefore, when re-dyed certain to appear spotty. We may here briefly refer to the different "appetite" for mordants and colours presented by different growths of wool. Two different wools treated in exactly the same manner with the same quantities of the same dye-wares do not necessarily take the same intensity, sometimes not even the same tone, of colour. The climate where the wool is produced, the breed of the sheep, the nature of their food, and possibly other causes have a modifying influence. Hence woollen manufacturers who pride themselves on the uniformity of their results are generally careful to use, year by year, the same growths of wool for the same class of goods.

The varying affinities of different kinds of cotton for colour have been pointed out in an earlier portion of the work: p. 28.

of ordinary precipitation, the mordant and the colour, each of them soluble, forming an insoluble compound together within the pores of the fibre, much as they would if mingled in a glass. Sometimes the mordant in a sufficiently dilute state is decomposed on coming in contact with the fibre, within which an insoluble oxide or sub-salt is deposited. In other cases insolubility is produced in consequence of the escape of some volatile acid; thus, when cotton is steeped in a solution of the acetate of alumina and dried, the acetic acid is volatilised, whilst the alumina with which it was combined remains in an insoluble state in or upon the fibre.

Hence we learn that such bodies only as are unstable in their constitution—their components being held together by but feeble affinities—can play the part of mordants. On the other hand, stable compounds do not readily yield up to the fibre any part of their constituents. Thus common alum is a stable salt, and, therefore, if used alone it is a feeble mordant. If it is converted into basic alum, whose ingredients are held together more loosely, its power is greatly increased. It must be remarked that the bases of mordants are not of a very decided basic character, but hold an intermediate position, and are capable of playing the part either of acids or bases, according to circumstances. Thus alumina and the oxides of tin can combine either with acids or with alkalies.

Many mordants if preserved for some time undergo spontaneous decomposition, an insoluble sub-salt being deposited, whilst a small portion of the base remains in solution in an excess of acid. This change is accelerated by dilution, by the application of heat, by exposure to light, and in some cases by the action of very low temperatures. "Nitrate of tin" is very unstable at an ordinary summer heat, whilst the nitrates of iron are often converted into a paste-like mass if exposed to intense frost.

There is a variety of opinion as to what is deposited upon the fibre by any mordant. Some consider that it is a hydrated oxide of aluminium, tin, or other metal. Others hold that the body thrown upon the fibre is a basic subsalt, retaining a certain quantity of the acid in which the tin, &c., may have been originally dissolved. This latter view is strengthened by the fact that the resultant shade is modified by the acid originally present. A sulphate of tin, or a chloride of tin, containing an admixture of sulphuric acid, gives with logwood a redder shade upon wool than is produced if a pure chloride of tin be applied, and this difference no amount of washing will remove.

One and the same mordant, however fully it possesses the attributes we have just described, does not suit equally well for all cases. What is efficacious upon an animal fibre may be useless or even hurtful if applied to vegetable tissues. Certain dye-wares, moreover, are suited to some particular mordants, and give unsatisfactory results with others. Thus with madder alumina is pre-eminently the mordant to be used, whilst with cochineal and lac dye tin has an indisputable superiority. Some acids deliver the metallic base more readily to one class of fibres than to another. Thus if a piece of any tissue, consisting of a mixture of cotton and woollen, be steeped in dilute nitrate of iron, a buff colour will be produced upon the cotton, whilst the wool remains practically untouched. If, on the other hand, a similar piece of cloth is soaked in dilute chloride of iron, the result is reversed, the iron being mainly deposited upon the wool.

The mordants for wool and worsted dyeing and printing are generally the most decidedly acid. Those for silk are more neutral, and in cotton dyeing and printing excess of free acid must be carefully avoided. On the other hand, cotton can be successfully mordanted with preparations, in which the solvent is an alkali, and the matter to be deposited on the fibre plays the part of an acid, such as the stannate and the aluminate of soda, which are advantageously used for cotton, whilst with animal fibres their applications are very limited.

Mordants are either applied preparatory to the colouring matters (the ordinary routine for cotton), along with the colours (the usual procedure for

wool), or, though less frequently, after the colour.

The metals which enter into the composition of mordants are aluminium, tin, iron, chromium, lead, copper, zinc, arsenic, mercury, antimony, and manganese. Bismuth, nickel, cobalt, tungsten, molybdenum; and magnesium have also been applied. Even sodium performs functions which can only be regarded as those of a mordant.

The acids employed are the nitric, hydrochloric, sulphuric, tartaric, oxalic, hyposulphurous, boracic, silicic, and phosphoric.

A. Mordants of Tin, technically known as "Tin-Spirits."

Tin is employed as a mordant in three different states of chemical composition, the protoxide, the sesquioxide, and peroxide, or their corresponding chlorides. The protoxide of tin, known also as stannous oxide, is a compound of the metal with the smallest possible quantity of oxygen. It forms with the acids colourless salts and solutions, which have a strong affinity for a further quantity of oxygen, and are hence powerful reducing agents. With alkalies, such as soda and potassa, it is also capable of playing the part of a feeble acid, forming compounds known as stannites.

The sesquioxide of tin is a body concerning whose nature and properties chemists are not agreed. Its compounds are of a reddish-amber colour, and are not permanent, passing, if kept for any length of time, into variable mixture of the other oxides, combined with whatever acids were present.

The peroxide of tin, known also as stannic oxide, stannic acid, binoxide of tin, contains the highest proportion of oxygen. Its salts and solutions, if the acids employed be perfectly pure, are colourless. Should, however, the smallest trace of iron be present they have a very faint yellow colour. The compounds of the peroxide of tin have an oxidising effect upon bodies with which they are brought in contact.

Generally speaking the proto-salts of tin are applied to wool, and the persalts to cotton. The sesqui-salts, the consumption of which is more limited, are used in certain cases to both. The compounds where tin plays the part of an acid, such as the stannites and stannates, are almost exclusively

restricted to cotton dyeing and printing.

The successful preparation of tin-mordants is a matter of great nicety, demanding close attention to certain minute particulars, which can scarcely be explained in writing. Purity of the ingredients used is a matter of vital importance. The tin should be the finest "grain-bar," the "lamb and flag" brand being generally the most satisfactory. The economy effected by the substitution of lower qualities, containing traces of iron, copper, arsenic, antimony, &c.,

is a poor compensation for occasional and costly failures. The like care must be taken in the selection of the acids employed. Traces of iron and of arsenic are very pernicious. The coarse hydrochloric (muriatic) acid obtained as a secondary product at the alkali-works, and known in commerce as "towersalts," is not trustworthy. It sometimes yields good results, but as frequently occasions mischief, the more serious as the cause is not readily detected. The hydrochloric acid employed should be "cylinder-salts," made from clean salt, and from sulphuric acid free from arsenic. The presence of sulphurous acid, of free chlorine, of arsenious acid, or arsenical chlorides, leads to annoying complications. Both the hydrochloric and the nitric acid used should be free from sulphuric acid, an agent which, indispensable as it is, should never be introduced except where directed, and then in exactly known quantities. The sulphuric acid employed should be prepared from Sicilian sulphur, and not from iron- or copper-pyrites, which contain arsenic in greater or smaller quantities. It should also be free from nitrogen compounds.

The following instructions will be of use in judging of the quality of the materials used in the preparation of tin mordants:—The tin should dissolve in pure hydrochloric acid without leaving a black powdery residue. If such residue appear it should be well washed in distilled water, dissolved in nitric acid, freed from excess of acid by evaporation, and mixed with an excess of

ammonia. A blue tinge indicates the presence of copper.

For the detection of arsenic and antimony a few fragments of the suspected metal are placed in a Marsh's apparatus, and dissolved in pure hydrochloric or dilute sulphuric acid. The gas given off is burned at the jet, with the precautions indicated in treatises on qualitative chemical analysis, and fragments of white porcelain are held in the flame. If shining metallic spots are deposited on the porcelain, either arsenic or antimony or both must be present.

As regards other impurities, a portion of the solution of the metal in pure hydrochloric acid is saturated with sulphuretted hydrogen gas, a current of which is passed into it as long as anything is deposited, and until the liquid has a strong and permanent smell of the gas. The precipitate formed, which may contain sulphurets (sulphides of tin, lead, copper, arsenic, and antimony), is filtered off, and digested in hydrosulphate of ammonia containing an excess of sulphur. Should any matter remain undissolved, which when dried and heated does not volatilise, it is probably sulphide of lead.

If zinc and iron are present, they will be found in the liquid filtered from the precipitate occasioned by the current of sulphuretted hydrogen. This filtrate is concentrated by evaporation to a small bulk, heated with nitric acid, and, after the excess of the acid has been expelled, it is mixed with ammonia. If iron is present it will be deposited as hydrated peroxide, of a reddish-brown colour. This is removed by filtration, and the residual liquid, after further concentration, is mixed with a solution of perfectly pure carbonate of soda. A white precipitate shows the presence of zinc.

Or the liquid as filtered from the precipitate obtained by sulphuretted hydrogen is mixed with hydrosulphate of ammonia. If any precipitate of fixed matter is obtained the tin contains iron, zinc, or some metal of the same class.

Hydrochloric acid, or, as it is still called, muriatic acid or "spirts of salts,"

is generally sold to dyers and printers at about 32° Tw. = sp. gr. r·60. When diluted with distilled water and mixed with a small quantity of a weak solution of chloride of barium it should not give a white precipitate or turbidity. If such appears the sample contains sulphuric acid, either from slovenly preparation or from design, and should be rejected. If a few particles of granulated tin are put in a test-glass and covered with the acid the gas given off should be free from the odour of sulphuretted hydrogen, and the resulting liquid should be clear, not yellowish or turbid. In the latter case the sample is contaminated with sulphurous acid, a very common impurity when the manufacture is not conducted with due care.

An ounce of the acid should be placed in a small porcelain capsule, and evaporated to dryness at a gentle heat. If pure nothing will remain behind. If, as is sometimes the case, common salt has been added to raise the specific gravity of a weak acid, a saline residue will be left in the capsule. To detect arsenical compounds a few fragments of absolutely pure zinc are placed in a Marsh's apparatus, and covered with the suspected acid previously let down to one-half its strength with distilled water. The gas generated is then

burned at the jet as directed in testing tin for arsenic.

Nitric acid, or, as it is technically still called, aquafortis, is sold for the preparation of mordants at two strengths. Double aquafortis varies in specific gravity, from 64° to 66° Tw., about 1.50 to 1.56. It may be tested for sulphuric acid, for saline matter, and for arsenical compounds, in the same way as directed for hydrochloric acid. In testing for arsenic, it should be previously diluted with four or five times its volume of water. Sulphurous acid is not likely to be present. Nitrate of soda is a not unfrequent adulterant. The action of nitric acid in dissolving metals is greatly modified by the presence of hyponitric and nitrous acids. These impurities may be removed by the addition of peroxide of lead or red-lead. Either of these bodies gives off oxygen, so as to convert the lower oxides of nitrogen into nitric acid, whilst the lead does not dissolve. The nitrous acid is, however, liable to be reproduced if the stock is left exposed to the light, especially to direct sunshine.

The so-called "single aquafortis," or dyers' aquafortis, is a quite peculiar preparation. Its strength is generally 32° or 33° Tw. It is absolutely free from sulphuric acid and from the lower oxides of nitrogen. To free it from this impurity various expedients are adopted at different establishments. Sometimes it is exposed to the air for several weeks in a cool dark place. Others cause it to trickle in a thin stream down stone-ware channels filled with clean quartz pebbles. In one large chemical-works, in Yorkshire, men are actually set to pour the acid from one receiver to another. Elsewhere a stream of cold air is forced through the tanks of acid, which has the effect of causing the nitrous and hyponitric acid to be expelled. Single aquafortis contains a certain amount either of hydrochloric acid or of an alkaline chloride. This is not to be viewed in the light of an adulteration, since without it the aquafortis would not answer its purpose in the preparation of "scarlet spirits."

Sulphuric acid, commonly known as oil of vitriol, or simply "oil," is generally bought for mordant-making as "double oil of vitriol,"—the strongest quality of acid which can be obtained by the ordinary process. It stands at 169° to 170° Tw. A variety of impurities may be present, which interfere

more or less seriously with the uses of this acid. Arsenious acid, which is often present, is detected by means of Marsh's apparatus, as directed for hydrochloric acid, the sulphuric acid being previously diluted with ten times its volume of water. Nitric oxide or other nitrogen compounds are also common, and may be detected by putting a little of the suspected sample in a test-glass, and dropping into it a clean fragment of the protosulphate of iron (copperas). If a trace of nitric oxide be present, a slight reddish-brown colouration will appear in the liquid, and will become by degrees more intense. Dry sulphate of soda (salt-cake) is sometimes added to increase the apparent strength of diluted acids. To detect it a portion of the acid is evaporated to dryness, when sulphate of soda, if present, remains behind.

The purity of the water is far from being an unimportant point. Rainwater, condensed steam-water, or the surface drainage of uncultivated moorlands, should be selected. Well- and river-waters, holding in solution lime,

magnesia, iron, or alumina, may produce serious mischief.

It must not, however, be supposed that purity of ingredients and strict attention to the proportions laid down in approved receipts will suffice to produce satisfactory results. The initial temperature, the order in which the materials are mixed, the speed at which the operation progresses, and the higher or lower degree of heat obtained in the process,—all modify the result. It is very easy to find two samples of a tin solution made with the same materials in the same proportions, yet where the one gives an excellent result the other is practically worthless, having affinity neither for the fibre nor for the colour.

I. Proto-Salts of Tin and their Solutions.

Protochloride of tin, or stannous chloride, unmixed with any other body, is used in dyeing and printing in various forms. These are tin-crystals, sometimes called tin-salt, or salts of tin; double muriate and single muriate. The preparation of these compounds is very simple. To obtain tin-crystals, hydrochloric acid, at 32° Tw., is allowed to act upon an excess of feathered tin, with the aid of heat. The operation is generally performed in large stone-ware vessels, heated by means of a water- or steambath, and fitted with covers to prevent needless waste of hydrochloric acid vapours, whilst allowing the hydrogen gas generated to escape. Some chemists use copper vessels for this purpose, which, so long as any tin remains undissolved, are not in the slightest affected by the acid. A very common arrangement is to effect the solution in a series of large three-necked receivers, connected together by stone-ware pipes, so that any acid escaping from the first receiver is caught and utilised in the next. The most economical arrangement on the large scale is that devised by Noellner, who places the feathered tin in stone-ware cylinders, allows water to trickle down through the mass from above, and drives in from below hydrochloric acid gas as it issues from the ordinary retorts in which it is generated. The saturated solution of tin, however obtained, is rapidly evaporated down, during which process some fresh granulated tin must be constantly kept in the liquid, otherwise oxychloride and bichloride of tin will be formed, and the properties of the preparation will be modified. The liquid, when sufficiently concentrated, is drawn off, and allowed to crystallise.

The crystals, which should contain 52 per cent of metallic tin, are white,

silky, dry, and smooth to the touch. They should dissolve in ten times their weight of distilled water, without turbidity, and if a few drops of pure hydrochloric acid be added no turbidity or precipitate should appear on the further addition of a solution of chloride of barium. If a white cloud or deposit is produced, sulphate of zinc, sulphate of magnesia, or some other sulphate, is present as an adulterant.

Chloride of zinc is also sometimes present. In such cases the sample grows damp on exposure to the atmosphere, more rapidly than do genuine crystals. To ascertain its absence a sample of the crystals should be dissolved in water, with the addition of a few drops of hydrochloric acid. A current of sulphuretted hydrogen is next passed through the liquid until it is fully saturated. The precipitate produced by this means is filtered off, and the filtrate evaporated down to dryness. If the sample was genuine no fixed residue will remain after exposure to a red heat. Should a fixed residue be found, then, if no sulphuric acid can be detected in the crystals, the presence of chloride of zinc is highly probable.

If it is required to find the amount of metallic tin present in a sample of tin crystals, or in any solution in which this metal is present as a proto-salt, the following volumetric method can be recommended:—

A standard solution of tin is first prepared, by dissolving, in pure hydrochloric acid, exactly 500 grains of pure tin. The solution is then made up with distilled water to the exact volume of 20 ounces.

A solution of iodine is next prepared in the following manner: -- 127 grs. of pure iodine and 180 grs. of pure iodide of potassium are weighed out and dissolved in 10,000 grain-measures of water, without the aid of heat. This solution is preserved in small, well-stoppered bottles. The iodine solution is next standardised. For this purpose such a portion of the standard tin liquid is measured off as may contain exactly 2 or 4 grs. of metallic tin. It is put in a beaker, and mixed with bicarbonate of soda in excess, along with double tartrate of potash and soda sufficient to keep the liquid bright. A little starch-liquid is then added, and the iodised solution is allowed to drop in from a burette until a permanent, though faint, blue tint appears in the glass. The number of degrees of the burette consumed indicate what measure of the iodine solution represents 1 gr. of tin. A known quantity-say 5 grs.-of the tin-crystals under examination must next be weighed out and dissolved in water, with the addition of a very little hydrochloric acid. Bicarbonate of soda and the double tartrate are then added as before. The starch-liquid follows, and the iodine solution is then dropped in, as above, till a faint blue tint makes its appearance. The amount of tin present in the crystals can then be easily calculated.

Double Muriate of Tin is often the subject of a misunderstanding. Some writers conceive that it is a bichloride or per-salt of tin. This is an error. After examining hundreds of samples from different makers, and as used in different establishments, we can affirm that it is a proto-salt of tin, differing from single muriate merely by being stronger and having a higher specific gravity, just as is the case with "double oil of vitriol" as compared with "single." Double muriate of tin ranges in specific gravity from 70° to 120° Tw., and contains from 2½ to 5 ounces of metallic tin to the pound of liquid. It is made in the same manner as tin-crystals, with the only difference

that the liquid is bottled off when the required strength has been reached without pushing it on to crystallisation. Some makers, instead of applying heat to promote the action of the hydrochloric acid upon the mass of feathered tin, pour on the acid, and after a few minutes run it off upon another similar quantity of tin. In a short time it is returned to the first lot, and by this alternating action the temperature is raised and the tin dissolved much more rapidly than if the acid were allowed to act without intermission upon one quantity of tin. In some establishments it is customary to use the hydrochloric acid at the strength of 32° Tw., whilst in others it is diluted with more or less water before being allowed to act upon the tin. In consequence, two samples of genuine double muriate, of the same specific gravity, but from different makers, may contain unlike amounts of tin. The lower the initial strength of the acid, the more metal must have been dissolved to raise the specific gravity to any given point.

Double muriate is frequently adulterated with sulphuric acid, sulphates of zinc and magnesia, chloride of zinc, &c. The price at which many samples are offered is in itself a sufficient proof of sophistication, being frequently less than the market-price of the tin which ought to be present in the genuine article. Few samples are met with which do not contain sulphuric acid in larger amount than can be accounted for by the possible presence of a little of

this body as an impurity in the hydrochloric acid used.

The methods for detecting these various sophistications have been indicated above. The weaker double muriates, from 70° to 90° Tw., are used by the woollen-dyers; the stronger, at 110° to 120°, are applied to cotton, which is less able to resist the action of acids.

Single Muriate of Tin is comparatively little used. Its specific gravity ranges from 40° to 60° Tw., and its proportion of metallic tin varies from 1 to 2 ounces per lb. It is chiefly employed in wool-dyeing.

II. Solutions of Proto-Salts of Tin, in which other Acids are used along with the Hydrochloric.

Old Scarlet Spirit	(Dr.	Ba	ncro	it's).		
Mix—Oil of vitriol					 2 lbs.	
Hydrochloric acid, at 32° Tw.					 3 11	
and dissolve in the mixture-						

Tin 14 ozs.

This spirit was, as its name implies, formerly used for lac and grain scarlets upon woollen and worsted goods. It is now little used, as the scarlets produced by its means are apt to exhibit a brownish shade.

Amaranth Spirit.

Mix-Hydr	ochlor	ic acid	l, at	32° T	w.	 	 	 95	lbs.
Oil of									
And dissolve-	_								
Tin						 	 	 4	" II ozs

This spirit is greatly recommended by some woollen-dyers for producing reddish-violet and purple shades with the woods.

Yellow and Orange Spirit.

Double muria						
Mix-Oil of vitriol	 	 	 	 	 2	1)
Water	 	 	 	 	 2	**

And when cool add the mixture to the double muriate. The more tin and the less free acid occur in the double muriate, the more the cloth will exhibit a beautiful greenish reflection if it be held up to the light, and the eye directed horizontally along its surface.

Another Yellow Spirit.

Hydrochloric acid, 3 parts; sulphuric acid, 1 part; water, 1 part; as much feathered tin as it will take up. The heat should not rise above 60° F.

Scarlet Finishing Spirit.

Take 3 pints muriate of tin, at 54° Tw.;

2 ozs. oxalic acid, dissolved in hot water sufficient to reduce the whole to 40° Tw.

This spirit, as its name implies, is used for "raising" or finishing grain scarlets which have been begun with the "bowl-spirit" or "scarlet spirit" described below, under the sesqui-salts of tin. It gives extreme fire and brilliance. Some dyers consider that a richer and mellower shade is obtained if half the oxalic acid above specified is replaced with tartaric. In some establishments this spirit is used at once along with grain or lac, without the preliminary application of the "scarlet spirit." This is especially the case when hard worsted trimmings have to be dyed. In such cases it is used without tartar. For softer goods it is better to increase the strength of the muriate of tin up to 60° or even 70° Tw. This is especially recommended for grain orange, maize, and similar shades.

Another Scarlet Finishing Spirit.

Take 16 quarts muriate of tin, at 54° Tw.:

I pint oil of vitriol:

3 lbs. water.

The sulphuric acid and water are mixed, allowed to cool, and then added to the muriate of tin: r lb. oxalic acid is next dissolved in ro lbs. water, and the solution is added to the other ingredients. When this spirit is used from the commencement in scarlet-dyeing, and not merely for finishing, tartar is required in the ordinary proportions.

Purple, Plum, or Puce Spirit.

Take good muriate of tin, at 70° Tw	
Mix sulphuric acid and water till the mixture stands at 28° Tw. When cool add of this	1
When cool add of this	i gal.
And stir well.	

Oxalate of Tin.—This name is very improperly used. A real oxalate of tin can scarcely be said to be known in commerce, but all mixtures of muriate of tin with oxalic acid, and with or without sulphuric acid, are sold under this name, often abbreviated into "Ox. Tin."

One of the most useful of these mixtures may be made by taking the above-mentioned purple spirit, and adding to it rounce of oxalic acid, previously dissolved in hot water, for every gallon. This oxalate of tin will then serve for finishing royal blues, for putting a top bloom on blacks, as a scarlet spirit with grain or lac, and as an orange spirit with mixtures of grain and flavin, young fustic, &c. If greater brightness is required, in case of scarlets or royal blues, the proportion of oxalic acid may be raised from rounce to real or 2 ounces per gallon. Such increase of oxalic acid is not recommended for topping blacks. This oxalate of tin makes the nearest approach to a universal spirit for wool-dyeing.

The following are oxalates of tin all in actual use:-

Muriate of tin, a							
Sulphuric acid, a	t 42°	Tw.	 	 			3 ,,
Oxalic acid			 	 2 ou	nces	per	gallon.

- b. Muriate of tin, at 76° Tw. 6 gals.

 Sulphuric acid, at 42° Tw. 4 ,,

 Oxalic acid 2 ounces per gallon.
- c. Muriate of tin, at 70° Tw. 6 gals.
 Sulphuric acid, at 40° Tw. 4 ,
 Oxalic acid 2 ounces per gallon.

Claret Spirit.

The bluest shades are produced by a pure muriate of tin, made by mixing 3 parts by measure of hydrochloric acid, at 32° Tw., with 1 part of water, and saturating it with tin up to 48° to 50° Tw. If to be used in rag-dyeing, for the conversion of blacks into clarets, 10 per cent of a solution of common salt in water, at 32° Tw., may be usefully added. The sulphuric acid which the rag-dyer uses will decompose the salt, forming sulphate of soda, while the hydrochloric acid liberated will aid in discharging the blacks. If redder or browner clarets are in request, there may be added to the muriate of tin from $\frac{1}{2}$ th to $\frac{1}{10}$ th by measure of dilute sulphuric acid, at 28° Tw.

The Chlorostannite of Ammonium, a compound of stannous chloride (protochloride of tin) and chloride of ammonium (sal-ammoniac), is prepared by heating tin-dust with sal-ammoniac. It forms regular octahedral crystals, which dissolve in water, the solution becoming turbid on boiling. Its uses

have been merely experimental.

The Stannite of Soda is a compound in which stannous oxide—the protoxide of tin—plays the part of an acid. It is formed by dissolving the precipitated hydrate of stannous oxide in a solution of caustic soda to saturation, and preserving the product, as far as possible, from contact with the air. It is at present rarely used.

III. Sesqui-Salts of Tin.

The sesqui-salts of tin are much less used, and even much less known, than either the proto- or the per-salts. They may be distinguished by their colour, which is of a peculiar deep amber or brownish-yellow. At low temperatures they are moderately permanent, but at an ordinary summer heat they are decomposed in about twenty-four hours. The best known compound of this class is—

Nitrate of Tin, called also, from its principal use, "Scarlet Spirits" and "Bowl-Spirits," because prepared in large stone-ware bowls. The name nitrate of tin, it must be remembered, is applied in some districts to per-salts of tin prepared with mixtures of nitric and hydrochloric acid, in which the latter largely predominates. The name, however, in the woollen regions of Yorkshire, and especially in the Halifax and Bradford districts, is exclusively applied to the compound we are now describing. Its preparation is a matter of some nicety. A known quantity of the liquid which we have mentioned above under the name of single aquafortis, or dyers' aquafortis, standing at 32° Tw., is placed in a capacious and perfectly clean bowl, and the finest grainbar tin, in the rod, i.e., not feathered, is dissolved therein, in the proportion of I lb. of metal to 8 lbs. of the acid. The number of rods put in at first is varied, according to the temperature and the make of the acid. If the weather be neither hot nor cold, and the acid of an average quality, some four or five rods are placed in each bowl, and allowed gradually to dissolve. After a time, if the operation is successful, the liquid is said to "turn,"—that is, to assume a deep amber or orange colour. When this point is once attained, all that is required is to feed in by degrees the remainder of the tin that has been weighed out, taking care that the action neither dies out from want of material nor becomes too fierce. No bubbles of red- or orange-coloured gas ought to be formed. If the process is unsuccessful, the liquid will sometimes remain colourless, like water, for two or three hours, and then suddenly become thick and turbid, without development of the amber colour. Under other circumstances, especially if too much tin has been added at the outset, orange-coloured fumes of nitric oxide are thrown off, and the tin, instead of dissolving, is deposited in an insoluble condition. In these cases the spirit is said to have "turned its back" on the operator, and is hopelessly spoiled. In cold weather as many as eight or ten rods may be entered at once without fear of accident; but when the temperature is high, two, or even one, may be quite sufficient, and it is sometimes needful to keep down the action by placing the bowl in a current of cold water. Sometimes, in hot weather, this spirit may be advantageously started with a small handful of clean, dry, feathered tin; rods being afterwards gradually added, when the spirit is once fairly in course of formation. The operation is greatly facilitated if, at the outset, half a pint of nitrate of tin, from a former making, is added to the aquafortis.

If properly made this spirit is a deep amber liquid, of from 58° to 66° Tw., and contains about 2½ ounces of metallic tin to the pound. It is not an article of commerce, being always made on the spot on account of its instability. On long standing it deposits its tin in a yellowish gelatinous mass, and becomes unfit for use.

Curiously enough, some persons have denied the very existence of this preparation, though known and used in every dye-house in Yorkshire where cochineal shades are produced. Almost the only author who admits its existence is J. Ordway ("Chemical Gazette").

Nitrate of tin-is chiefly used for grounding searlets and other cochineal shades upon wool and worsted goods of all kinds. It is sometimes also employed in cotton-dyeing, especially for the cotton warps of coburgs, delaines, and other mixed goods.

Purple Spirit for Wool and Worsted.

The following spirit is used in producing certain purples with mixtures of logwood and the red woods:—

Take common nitrate of tin, which should be well made and recent. Warm it gently, by setting the bowl containing it in a larger cistern or vessel of hot water, and add as much grain-bar tin, in the rod, as it will take up. It should mark about 80° Tw.

So-called "Aniline Spirit," known also as "Nitro-muriate of Tin,"—a name which is promiscuously applied to the results of at least a hundred different receipts having little in common, save that tin is dissolved in hydrochloric acid, to which more or less nitric acid has been added.

The mordant in question serves for working aniline colours upon the cotton warps of mixed goods, and also for certain fine browns, clarets, maroons, &c., produced with the woods. When well made this spirit gives very full, rich, bloomy shades,

Mix the acids, and enter about twelve rods at once, distributing them at regular intervals around the sides of the bowl. As these dissolve make further additions gradually, not letting the mixture get very hot. If the temperature threatens to become excessive, some of the partially dissolved bars of tin may be withdrawn from the liquid for a time, to moderate the action. If properly worked it will be of a reddish or deep amber colour. This spirit contains nearly 2 ounces tin to the lb. of acid.

The following receipts, of foreign origin, will, if carefully worked, yield compounds of the sesquioxide of tin.

Hellot's Mordant.

Nitric acid (streng	th not	given		 	 	8 ozs.
Water				 	 	8 ,,
Sal-ammoniac				 	 	$\frac{1}{2}$ OZ.
Nitre				 	 	2 drachm
Tin, granulated				 	 	I OZ.
		Anoi	her.			
Nitric acid				 	 	ı lb.
Water						
Sal-ammoniae						
Tin				 	 	2 ,,
		Anoi	her.			
Nitric acid, at 30°	Baum	ié		 	 	ı lb.
Sal-ammoniac				 	 	2 OZS.
Water				 	 	4 ,,
Tin				 	 	4 ,,

Whenever sal-ammoniac (chloride of ammonium) is added to a mordant, a certain amount of pink salt (see below) will be formed, and the result will differ from that given by free hydrochloric acid or chloride of sodium in equivalent amount.

IV. Stannic Salts, or Per-Salts of Tin.

These compounds, very extensively used in cotton- and silk-dyeing and in printing, are composed of the peroxide (binoxide or tetroxide) of tin, united with various acids, and of the stannic chloride or perchloride of tin. They are produced in a variety of ways, sometimes directly from the metal, and at other times by the oxidation of the proto-salts of tin, whether by means of free chlorine or of nitric acid.

The making of these preparations is a matter requiring much care, especially in all those processes where a mixture of nitric and hydrochloric acids is allowed to act upon the metal or upon proto-salts. According to the temperature employed and the speed at which the operation has been conducted, two lots, composed of the same materials, may contain very different proportions of protoxide and peroxide. The result may be in one case a perfect peroxide, whilst in another the proto-salt may largely predominate. Such varying compounds yield, of course with the same dye-wares, different shades of colour, to the great discomfiture of the dyer, who, using what he supposes to be identical materials, finds ever-fluctuating results. The condition or state of oxidation of a sample may be very easily detected. If to a little of the spirit placed in a test-glass we add a few drops of a solution of mercuric chloride (corrosive sublimate) in water, then, if any of the tin was present in the state of a proto-salt, a white turbidity is formed, which speedily blackens. If the tin be a pure per-salt there will be no apparent action.

But whilst the process should be brisk enough to ensure the formation of a perfect per-salt, as the only way to secure constant results, too rapid an action, and a consequently excessive temperature, can occasion serious mischief. The tin, in great part or entirely, instead of becoming dissolved, may be deposited at the bottom of the vessel as an insoluble peroxide. This result, known as "firing," is common in careless or inexperienced hands.

But without precipitating the tin in this insoluble state, its affinity for the fibre may be destroyed by a small excess in temperature. A spirit thus spoiled, if compared with one of the same class and made from the same materials, but in proper condition, shows no tangible difference. They, too, agree in specific gravity, colour, smell, in degree of acidity, and in the amount of tin contained; yet the one attaches itself readily to the fibre, which then, in contact with the colouring matter, dyes up a full shade; the other, similarly treated, yields merely an irregular and impoverished stain. It would seem, in consequence, that the per-salts of tin may exist in at least three different states, in one only of which they have a marked affinity for animal and vegetable fibres, and can be, by them, withdrawn from solution.

The acids present along with the per-salts of tin are chiefly the nitric and hydrochloric; the sulphuric is rarely used. Oxalic acid is also less frequently added than with the protosalts of tin. Alkaline chlorides and nitrates are not unfrequently present, and have modifying effects, especially the chloride of ammonium (sal-ammoniac), which forms with the stannic chloride a definite compound, to which we shall return below. The nitric acid used in preparing these compounds, except where otherwise specified, is the "double aquafortis" of commerce, of about 64° to 65° Tw. The tin is generally used not feathered or granulated, but in the rod.

Bichloride, Perchloride, or Tetrachloride of Tin, Stannic Chloride, Chlorostannic Acid, or Fuming Spirit of Libavius.—This compound, in its dry or anhydrous state, is used, not as a mordant, but in the preparation of one form of magenta. It may be obtained by slowly passing chlorine gas into a retort containing tin-foil or melted tin. The compound, as formed, distils over into a receiver, which is kept carefully cooled. It may also be obtained by distilling I part by weight of tin with 5 parts of mercuric chloride, or by distilling dry common salt with dry stannic sulphate (persulphate of tin) in an iron retort, raising the heat as long as anything passes over. It is a thin colourless liquid, which gives off dense white fumes on exposure to the air.

Aqueous Bichloride, or Stannic Chloride of Tin, known in some districts as "Scarlet Spirits," in others as "Dyers' Composition," and as "Hydrochlorate of Stannic Oxide," is made in a variety of manners, indicated above. Sometimes a double muriate of tin, at 120° Tw., or upwards, is saturated with chlorine gas, prepared by gently heating black oxide of manganese in hydrochloric acid. Some makers heat tin crystals to which a quantity of hydrochloric acid has been added, with nitric acid introduced by portions, carefully avoiding excess. Or the metal itself is dissolved in aqua-regia, avoiding excess of nitric acid, and conducting the process slowly. Nitric acid, when used in this manner, either along with tin-crystals or with the metal, is never entirely driven off. Whenever, consequently, bichloride or perchloride of tin, or hydrated stannic chloride, or "composition," is directed to be used, either alone or as one ingredient in a compound mordant, the article to be employed is that prepared by the action of chlorine gas upon tin-crystals or double muriate of tin. The chlorine should be allowed to act until a portion no longer gives the above-mentioned precipitate with a solution of corrosive sublimate. This pure aqueous perchloride of tin, either with or without the addition of oxalic acid, may be used for dying cochineal or lac scarlets with satisfactory results.

1. Red Cotton Spirits, known also as Crimson Spirits.

	_
Muriatic acid, at 32° to 34° Tw	 . 7 gals.
Nitric acid (double aquafortis), at 64° Tw.	 I gal.
Water	 . T

Mix these liquids thoroughly, and when they have stood for a few minutes enter the tin, 6 lbs. of which have been weighed out for the above quantity of acid, as follows:—Put in about six rods, upright, at equal distances around the sides of the bowl, and as they dissolve add the rest by degrees. It must never get hot enough to give off orange vapours. If the weather is very cold, eight or ten bars may be put in at first. In eight or nine hours all the tin will be dissolved. Never stir it whilst working. When finished it should be clear, and of a very pale straw-colour. In cold weather, the water mixed with the acids may be reduced to 3, 2, or 1 quart, or omitted altogether. This spirit is recommended for reds, crimsons, scarlets, clarets, browns, and sometimes drabs, upon cotton-yarns; and for reds, crimsons, and scarlets, upon the cotton-warps of mixed piece-goods.

2. Red Cotton Spirit.

Hydrochlo	ric ac	id, a	as be	fore	 	 	 	6 gals.
Nitric acid					 	 	 	r gal.
Water					 	 	 	ı ,,
Tin								6.1hc

Work as before. This spirit is more adapted for the cotton-warps of clarets and browns.

3. Red Cotton Spirit.

Hydrochloric acid, at 32° Tw.	 	 	 6 gals.
Nitric acid, at 64° Tw	 	 	 2 ,,
Tin			
Work as above.			

4. Red Cotton Spirit.

Hydrochloric acid, at 35°	Tw							81	gals.
Nitric acid, at 64° Tw.								Il	2.2
Tin sufficient to bring up	the	spe	cific	gra	vity	to !	540 7	w.	
Bichromate of potash								I)2.

5. Red Cotton Spirit.

Hydrochloric acid, at 32° Tw.	 		 3 gals.
Nitric acid, at 64° Tw	 	٠.	 I gal.
Water	 		 I ,,

Tin, 2 ozs. per lb. of the mixed acid.

In this case, exceptionally, the tin is not used in the bar, but granulated, and added in very small quantities at a time.

6. Red Cotton Spirit.

Hydrochloric acid, at 32	° Tw.	 		6 gals.
Nitric acid, at 64° Tw.		 		I gal.
Tin, grain-bar		 	 .]	to lbs.

Barwood Spirit.

Hydrochloric acid, at 32°	Tw.	 	 	 5 gals.
Nitric acid, at 64° Tw.		 	 	 I gal.
Tin, I oz. per lb. of mixed	l acids.			

Plum Spirit.

Hydrochloric acid, as above			 	 	6 gals.
Nitric acid, as above			 	 	I gal.
Tin, 11 ozs. per lb. of mixed	acid	ls			

Pink Spirit, with peach-wood or cotton; see "Yellow Spirit."

"Solution of Tin."

These preparations, called often simply "Solution," are used for similar purposes to red cotton spirits. They are generally a little stronger.

Hydrochloric	acio	lat	32° 7	Γw.	 	 	 6 gals.	
Nitric acid at	64°	Tw.			 	 	 11 gals.	
Water					 	 	 ı gal.	
Tin, in rods					 	 	 7 Ibs.	

Work in the same manner as directed for red cotton spirits. Let the action be brisk, and the surface of the liquid be covered with *fine* froth, but no orange vapours must rise.

This preparation is strongly recommended for the cotton warps of clarets, maroons, browns, &c.

No. 2 Solution.

Hydrochloric acid at 32° Tw.	 	 	 6 gals.
Single aquafortis at 32° Tw.	 	 	 3 gals.
Tin, in rods	 	 	 rol lbs.

Work gradually. Much recommended for similar purposes, and for drawing aniline colours upon cotton warps.

Purple Cotton Spirit.

Hydrochloric acid (as above)	 	 	 5 lbs.
Nitric acid (as above)	 	 	 ı lb.
Tin, 2 ozs, per lb, of acid.			

When dissolved add 4 ozs. of bichromate of potassa, previously dissolved in water, to every 18 gals. of the spirit.

Oxymuriate of Tin.

Hydrochloric	acid									20	lbs.	
Nitric acid										20	lbs.	
In which latter 5 lbs.	sal-a	mmo	niac	have	been	di	ssolv	ed.	Th	ien '	work	in—
7C.											11	

Ditto, No. 2.

Melt 16 lbs. tin crystals in a bowl set in a tank of hot water, and add gradually nitric acid, 20 lbs.

Ditto, No. 3.

Melt 60 lbs. tin crystals and I quart water by the heat of a water-bath. Then add by degrees 92 lbs. nitric acid at 60° Tw.

Ditto, No. 4.

Hydrochloric acid at 34° Tw.	 	 	 II lbs.
Nitric acid at 62° Tw	 	 	 5 lbs.
gradually 2 lbs, feathered tin.			

These oxymuriates are chiefly used by printers. The second is used for "cutting" madder pinks, and the fourth for spirit colours.

Pink Salt is a compound of stannic chloride (perchloride of tin) with chloride of ammonium. On mixing concentrated solutions of its two constituents it falls as a white powder. In many cases it is not used preformed, but its constituents are separately added to a colour. Pink salt has the power of dissolving a great number of organic colouring matters, and its applications in the tinctorial arts will doubtless become more numerous.

The peroxide of tin is also capable of playing the part of an acid. In this state it is called stannic acid, and forms stannate of soda, otherwise known as "preparing salt." It is sometimes made as wanted by adding a saturated

lye of caustic soda to a concentrated solution of perchloride of tin till the precipitate which falls at first is all re-dissolved. It is then, of course, mixed with the chloride of sodium. It may also be prepared in the dry way. Greenwood and Mercer obtain it by taking 22 lbs. of caustic soda (1 gallon weighing 13½ lbs.), and putting it in an iron crucible heated to low redness by a fire under it. When watery vapours cease to come off they add 8 lbs. nitrate of soda and 4 lbs. of common salt. When the whole is at or near the point of fusion 10 lbs. of feathered block tin are added and stirred with an iron rod until deflagration takes place, and the mass becomes fully red hot and of a pasty consistence. It may be purified by dissolving it, when cold, in water, allowing impurities to settle, decanting off the clear liquids, and evaporating it down to near dryness.

Young heats finely ground tin ore of good quality along with caustic soda to about 600° F.; or with nitrate and muriate of soda (common salt), a current of steam being passed at the same time over the mass. Purification by solution in water and settling, and subsequent decantation and boiling down

are here necessary.

Haeffely places in an iron pan litharge or red-lead (or hydrated peroxide of iron, hydrated peroxide of manganese, manganate of soda, indigo, &c.) and a solution of caustic soda containing 22 per cent of alkali. A plumbate or plumbite of soda is thus formed, heat being applied to hasten the process, and the air being as far as possible excluded. Feathered tin is then suspended or thrown into the liquid, when it dissolves, forming stannate of soda, whilst metallic lead is thrown down in a spongy state. The proportions are—16 lbs. tin, 45 lbs. caustic soda at 70° Tw., and 70 to 80 of litharge, or 54 lbs. of red-lead. When the tin is perfectly dissolved, which may require four to five hours boiling, the fire is withdrawn, and the sediment allowed to settle, and the clear liquid is decanted, and is ready for use. The deposit of spongy lead may be re-converted into litharge or red-lead by prolonged exposure to the air at a heat just below redness, and may be then used for another operation.

To ascertain the amount of tin present in a commercial sample of stannate, a small portion is dissolved in water, to which a few drops of hydrochloric acid have been added, and a few pieces of sheet zinc, pure and clean, are placed in the mixture. The tin is thus precipitated in a spongy metallic state. It is collected, washed with distilled water, re-dissolved in pure hydrochloric acid,

and its amount is determined as explained above.

Some dyers and printers believe that they can ascertain the value of a stannate by dissolving a known weight in a fixed measure of water, and noting its specific gravity as shown on Twaddle's hydrometer. This test is quite fallacious, since an adulterated article will raise the specific gravity of water as well as one of the best quality. Manufacturers of spurious chemicals are, as a rule, inclined to appeal to the hydrometer as a test of value.

Stannate of soda may contain an excess of alkali as well as silica, &c., from careless workmanship, and it may be intentionally sophisticated with common salt. The percentage of water in a hydrated or crystalline stannate is from 20 to 27 per cent. Salt is sometimes present to the amount of 28 per cent.

Stannate of soda is used in printing to prepare the cloth for receiving the so-called steam-colours. The calico is then passed through very dilute

sulphuric acid, which, combining with the alkali, leaves the stannic acid (oxide of tin) deposited in the fibre.

In dyeing cotton yarn is extensively used for a variety of colours, especially for the anilines. Its application to the warps of mixed piece goods requires much caution. The sulphur present in the wool or worsted is very apt to react upon tin presented in an alkaline solution, thus turning the fibre an unpleasant brownish colour. The only way of avoiding this mischief is to work at the lowest possible temperature, to make the solution very dilute, and not needlessly to prolong the mordanting process.

Some printers consider it advantageous to form double salts of the stannic and some other acid, and to employ them in place of the ordinary stannates. Mercer and Blyth patented the arsenio-stannates and phospho-stannates of potash, soda, and ammonia. The arsenio-stannate of soda can be made by dissolving 1½ lbs. of the arseniate of soda in 1 gallon of stannate of soda liquor at 50° Tw. The benefit to be derived from such admixtures or compounds is somewhat doubtful. In 1852 James Higgin patented an alumino-stannate to be used in place of the ordinary stannate. This alumino-stannate is prepared by adding to stannate of soda in solution, aluminate of soda also in solution, in such proportion that for every 14 lbs. of metallic tin in the stannate there shall be 1 lb. of alumina. The patentee proposes also to add chloride of aluminium to the chlorides of tin used in printing or dyeing.

Silico-stannates have been used experimentally, but the results were unsatisfactory.

Alumina Mordants.

Several compounds of aluminium are highly important as mordants. The majority of these have been incidentally described in the foregoing chapters, as potash-alum, ammonia-alum, sulphate of alumina, acetate of alumina, nitrate of alumina, muriate of alumina (aluminic chloride) oxalate of alumina, hyposulphite of alumina, &c. Tartrate of alumina is rarely used as such, but it is formed in the dye-bath whenever alum and cream of tartar are used together.

Aluminate of Soda, called also alkaline-pink mordant, was formerly prepared when wanted by adding an excess of caustic soda to a solution of alum or of sulphate of alumina. The mixture is kept at a boil until the precipitate formed at first is entirely re-dissolved. Sulphate of soda, and, if common alum was used, sulphate of potash, were always present. It is now sold in the solid state, and containing very little foreign matter. As its name implies, it is used by printers as a mordant for pinks. The calico, after treatment with the aluminate, is passed through a solution of chloride of ammonium or chloride of zinc, by the action of which alumina is deposited on the fibre.

Aluminate of soda is as yet little used among dyers. Though alkaline it is capable of fixing colours upon wool, which cannot be blackened by the reaction, as in case of the stannates and plumbates. Indeed, with judicious management the aluminate of soda can be made to produce every effect derivable from alum, and, in addition, certain others, which the latter is incapable of yielding.

Aluminate of potash is similar in its action to the soda salt, but being more costly is rarely used. Mixed with oil it has been proposed as a mordant for cotton to be dyed with madder. The shades obtained were fast but dull.

A double chloride of aluminium and ammonium applied to cotton yields with the woods a variety of browns, such as cinnamon and Esterhazy. It would probably repay a closer investigation.

Iron Mordants.

Copperas (Green Vitriol, Protosulphate of Iron, or Ferrous Sulphate) is generally manufactured from the soft whitish iron pyrites, or sulphuret of iron found in the coal measures, and familiarly known as "brass lumps." When exposed to air and moisture the latter is decomposed, hydrogen gas escaping, and oxygen being absorbed, whence the sulphide of iron is converted into sulphate of ferrous oxide. As the amount of sulphuric acid generated by the oxidation of the sulphur is often more in quantity than the iron is able to saturate, old iron of all kinds is added to the liquid, which drains from the heaped-up beds of pyrites. Copperas forms semi-transparent crystals of a pale greenish-blue, and contains 45 per cent of crystalline water, on the expulsion of which, by careful heating, a white powder remains, harsh to the touch. The crystals of copperas dissolve in about 12 parts of cold, and in one-third its weight of boiling, water. At common temperatures it oxidises and turns brown, being partially converted into ferric sulphate (sulphate of the peroxide of iron). This change takes place the more readily in proportion as the copperas and the air are damp, and as the crystals have been formed from a neutral solution. Copperas should be chosen well drained from the mother-liquor, forming bold, hard, clean crystals of a decided green colour. If it is soft, dull, and of a whitish or greyish green, known in the trade as "milky," the presence of alumina is to be suspected. To ascertain this point a small portion is dissolved in water, and boiled with pure nitric acid. To this liquid, whether clear or not, a large excess of pure caustic soda, preferably that prepared from metallic sodium, is added. The whole is digested in a clean, covered iron vessel, diluted with distilled water, and filtered. If a white precipitate appears on adding to the clear filtrate a solution of pure sal-ammoniac, the copperas contains alumina. Most commercial samples will be found to contain this impurity to a trifling extent. If the pyrites employed have been ill selected and are contaminated with alumshales, or if the copperas has been crystallised from a highly concentrated solution, sulphate of alumina may be present to a very serious extent, and may render the copperas practically worthless. The presence of alumina must be regarded rather as the result of mismanagement than of intentional fraud. Zinc and copper are rarely present, and never, probably, in injurious doses. The latter might be very readily detected by dissolving a little of the sample, boiling with nitric acid, and adding to the liquid ammonia in excess. The precipitate which subsides is then filtered off. If the clear filtered liquid shows a blue tinge, copper is present. Lime is sometimes dusted over copperas to give it a brownish appearance, for which some consumers have a preference. The applications of copperas in dyeing and printing are less extensive in the present day than was formerly the case. In producing logwood blacks upon wool it has been largely replaced by the bichromate of potassa, at the cost, it is true, of the stability of the resulting shade. For saddening olives, drabs, clarets, &c., and for cotton blacks, it has been generally discarded in favour of a nitrate of iron. Some dyers are very partial to an article sold as "calcined copperas," the value of which is very doubtful. If the copperas has been really calcined it is reduced to an insoluble powder, which will subside to the bottom of the beck, and will have no more influence on the dyeing process than an equal weight of sand. If the crystalline water has been merely expelled by heat the salt will instantly return to the hydrated state on contact with water. The solutions of the dry and of the crystalline salt must be absolutely identical.

Persulphate of Iron (Ferric Sulphate, or Red Sulphate of Iron.)—This salt contains iron in the state of peroxide (ferric oxide), instead of protoxide as in copperas. It may be prepared by heating 30 lbs. of hydrated ferric oxide of iron, 70 lbs. of red oxide of iron, and 150 lbs. of oil of vitriol. Or a solution of green vitriol is mixed with half as much sulphuric acid as it already contains, and then heated with nitric, in small quantities, till all the iron is peroxidised.

Persulphate of iron is in the mass a yellowish body, and dissolves in water with a pale yellow colour. In the anhydrous state it is a white powder. Persulphate of iron is rarely manufactured and used in a state of purity, but it forms a considerable part of many of the mordants sold under the name of nitrate of iron.

Muriate of Iron (Solution of Protochloride of Iron, or Ferrous Chloride).

—This mordant is made by dissolving scrap iron in hydrochloric acid, keeping the metal in excess. It very readily takes up oxygen, and suffers decomposition if exposed to the air, whence it should be kept in well-stoppered bottles. It generally is sold at about 80° Tw. If concentrated it deposits pale green crystals, which must be carefully kept from exposure to the air, and which are sometimes preferred to the liquid. They are deliquescent, and easily become peroxidised. Muriate of iron is not extensively used. It assists in the production of certain catechu drabs and slates, and is sometimes employed along with salts of manganese.

Permuriate of Iron (Solution of Perchloride, or Ferric Chloride) is made by dissolving metallic iron in a mixture of nitric and hydrochloric acids. It is

very rarely used.

Black Liquor (Acetate of Iron, sometimes called also Black Mordant).— The properties, preparation, and uses of this important mordant have been incidentally described in speaking of madder (p. 290).

Nitrate of Iron.—This name is somewhat promiscuously applied to an entire class of compounds which differ widely in their composition, their preparation, and their uses. They may be divided into three classes, known as "blue," "black," and "saddening" or "common," irons. The first-mentioned are used for dyeing blues upon cotton or upon silk (the latter less frequently since the introduction of the aniline blues) with the aid of prussiate of potash (ferrocyanide of potassium).

Black irons serve for dyeing or printing blacks upon cotton, and to a less extent upon animal fibres, along with myrobalans, divi-divi, galls, sumac, logwood, &c. Common or saddening irons are employed for "saddening" drabs, browns, clarets, &c.

Some nitrates of iron are really what the name implies, compounds of nitric acid with iron, the latter being, as a rule, entirely in the state of peroxide. Others are mixtures, in the most variable proportions, of the true

nitrate and of the sulphate of iron, and in others acetic acid is present, as well as the nitric and sulphuric. In specific gravity nitrates of iron range from 40° to 120° Tw. Some of the varieties are prepared from copperas, some from scrap iron, and others from both. Previously made nitric acid is used in some cases, whilst in others the iron is dissolved by nascent nitric acid, generated by the action of sulphuric acid upon nitrate of soda.

Taking first the "blue" irons, used for dyeing Prussian blues upon silk or cotton, we find that they are "sharper" than the "black" and "common" irons. They contain, in other words, a relatively larger amount of acid and a smaller of iron. If they are too "dead"—that is, if the proportion of iron be too great—a large part of the colour formed will be deposited, not on the fibre, but at the bottom of the dye-beck, and the part which is fixed upon the goods will be uneven, flat, and loose. Still the blue nitrate of iron must not be too raw, or the shades resulting will be meagre, and the fibre will be in

danger of being "tendered" by the free acid.

For dyeing cotton-yarns or unmixed cotton piece-goods, a blue iron made from copperas, and brought as closely as possible to a perfect per-salt, will give shades superior to a pure nitrate made by the action of aquafortis upon scrap iron. The following formula will give satisfaction:-Put into a large cask, capable of holding at least 130 gallons, 5 cwts. of dry, clean copperas. Pour upon it 130 lbs. of double aquafortis (nitric acid, at 64° Tw.), and stir the whole well together, so that every part of the copperas may come in contact with the acid. During this operation care must be taken to avoid the suffocating fumes which are given off in great quantities. On this account the manufacture of nitrate of iron is best carried on in open sheds where the wind may have free play, or under a hood, connected with a chimney having a powerful draught. At night the mixture is thoroughly stirred up again. The stirring should not be too violent. The operator should avoid hasty circular movements, and try, instead, to turn over every portion of the copperas, thrusting his pole to the very bottom, and working as if groping with the end for some lost article. The stirring is repeated the second day, morning and night, and on the morning of the third day; the third night it will be finished. The copperas, if the operation has been successful, will be found entirely consumed, or perhaps a few pounds may remain at the bottom of the cask. It is then let down with water to about 70° or 80° Tw., well stirred up, allowed to settle, and drawn off into carboys. If the ingredients are good, and the process has been carefully conducted, the resulting liquid will be clear and bright. It is, of course, a nitro-sulphate of the peroxide of iron. If any of the copperas has not dissolved in the nitric acid, but has been merely taken up by the water added for dilution, a small quantity of proto-salt of iron (sulphate) will be present. This iron, if preserved from light and from extremes of temperature, keeps well. Still, especially in summer, it is not advisable to make more than a fortnight's consumption at once.

If mixed piece-goods with a cotton warp, such as coburgs, delaines, &c., have to be dyed blue, and if the worsted has first been got up to the required shade with one of the aniline blues, a blue nitrate of iron made from copperas is not admissible, since it works to some extent upon the worsted as well as upon the cotton, and injures the tone of the former. If a light or sky-blue is intended, or if the blue is to serve as the basis of a green, the following

receipt may be followed:—Let down ordinary double aquafortis to half-strength (32° Tw.) with water. Add to this gradually scrap iron, which should be clean and free from rust, so long as it is dissolved briskly with rise of orange fumes. It will stand at 43° Tw.

If a deeper blue, of a rich "bloomy" tone, is required, either of the two following receipts will serve the purpose:—

Pour the water upon the nitrate of soda, and stir to promote solution. When dissolved, add the acid and the iron by degrees, not letting the mixture get too hot.

 No. 2. Nitrate of soda
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 .

Mix the ingredients as above stated, and keep up a steady action, taking care not to let the heat get excessive. It is generally preferable not to add the whole of the oil of vitriol at once.

Both these "blue irons" are unstable, and if kept many days are apt to deposit a large amount of sediment.

In "black irons" perfect saturation of the acid is a matter of great moment. In black-dyeing no substance is employed which, like the prussiate of potash, is able to neutralise any excess of free acid, which, if present, damages the colours, the goods, and, in case of printing, the colour-doctors, and even the copper cylinders. Still it is needful to avoid the opposite extreme, for if the nitrate is overloaded, so that the oxide of iron is not slowly and regularly delivered to the fibre, the goods will, when completed, appear spotty and cloudy, or may even be smeared with buff patches, where oxide of iron has been deposited too irregularly and rapidly to combine with the tannin. For blacks, as a general rule, a nitrate of iron made from copperas is preferable to one prepared from the metal. The receipt given above for a blue iron for cotton skeins will serve very well for blacks, the nitric acid, for the weight of copperas given, being reduced to 120 lbs.

For blacks, it is not necessary that the whole of the iron should be peroxide. Better shades can, in fact, be produced with a nitrate of iron in which a proportion of proto-salt is still present. The result of the process, as worked with the above modification, is diluted with water to about 50° Tw., if for dyeing, but to 80° if for printing.

Some makers add to black nitrate of iron a certain amount of brown sugar of lead, which should not exceed 95 lbs. to 138 lbs. of the copperas originally used. The result is that the oxide of lead combines with its equivalent of the sulphuric acid present, and falls down as insoluble sulphate of lead, whilst the acetic acid, formerly combined with the lead, seizes upon the oxide of iron in its room. Should, however, any excess of nitric acid be present, this seizes the iron in preference to the acetic acid, a portion of which remains free. As free acetic acid is much less injurious to fibres and to colours than free nitric

acid, such a nitrate of iron is less likely to prove dangerous. Hence nitrates, with the mixture of acetate, are sometimes used as Burling Irons, for the following purpose:—In dyeing woollens a black, or indeed other shades, it is very commonly found, when the goods leave the dye-beck, that they are sprinkled over with small specks which have failed to take the colour, and have remained white, or rather a dirty grey. These spots—technically called "burls"—are caused by portions of cotton which have become intermixed with the wool, and which, not having the same affinity for colours as the wool, escape undyed. In case of black goods, if these spots are very numerous, the pieces are submitted to a formal cotton-dyeing process, with an astringent and with nitrate of iron. In the selection of the latter much care is required. If too sharp it alters or destroys the shade of the wool. If the iron is in excess the goods will be disfigured with rusty stains. The above-mentioned black iron, with the addition of acetate of lead, is preferred by many practical men for this purpose.

The "common" or "saddening" irons are sharper than those used for black dyeing, in order that the oxide of iron may be deposited very slowly, and may combine more firmly with the tannin of the sumac, myrobalans, &c., and may the better resist treatment with alum or tin mordants. They are, as

far as possible, perfect per-salts of iron.

The following receipt is in extensive use:—Prepare a nitrate of iron by the process given for "blue irons" on cotton-yarns. The weight of nitric acid to 5 cwts. of copperas may be 130 to 135 lbs. After the iron has been worked as above directed, the liquid is run off from any residue of undissolved copperas, and then diluted with water. By this means no unconverted protosulphate of iron is dissolved as such and mixed with the nitrate of iron.

Common Iron for Drabs.

Let down nitric acid (double aquafortis) to 34° Tw., and of it take 100 lbs. Dissolve in it 4 lbs. of clean scrap iron. Then add by degrees as much copperas as it will take up, which will be about 84 lbs. Let it down with water to about 60° Tw.

Muriatic acid should never be used in the manufacture of nitric acid. The nitric acid employed should be free from this impurity, and if nitrate of soda is used it should be freed from common salt by re-crystallisation. Muriatic acid not only retains the iron more tenaciously than nitric, but delivers it upon animal fibre.

In examining samples of nitrate of iron the following instructions may prove useful:—Mix a portion with pure hydrochloric acid, and dilute with distilled water. If a white precipitate is formed on adding a solution of chloride of barium, sulphuric acid is present. This shows either that the sample has been made—wholly or in part—from copperas, or that sulphuric acid, as such, has been added. Dilute another portion of the sample slightly with distilled water, and add pure ammonia in excess. Filter off the precipitate, evaporate the clear filtrate to dryness, and heat the residue to redness in a small porcelain capsule. If any fixed matter remains the sample has been got up with nitrate of soda. Another portion is diluted with distilled water, a few drops of pure nitric acid being added to prevent turbidity. A solution of nitrate of silver is then added. If a white curdy precipitate is formed, either some

hydrochloric acid (muriatic acid) is present, or, if nitrate of soda has been found, it may have been contaminated with common salt.

To detect alumina, a little of the sample is boiled with a mixture of nitric and hydrochloric acids, to peroxidise any iron that may have remained in the state of protoxide. Pure caustic soda (prepared from metallic sodium) is dissolved in a little water, and added to the sample thus treated in decided excess. It is then boiled in a clean iron vessel, and filtered. To the clear filtrate a solution of chloride of ammonium is added. If a white precipitate appears alumina is present.

In order to determine whether any part of the iron present in a sample is in the state of protoxide or not, a solution of carbonate of soda is slowly dropped in. If the sample is a pure peroxide salt, all the iron present being brought to the highest state of oxidation, the precipitate formed will be uniformly pale yellow. If any protoxide be present a greenish or olive turbidity will appear in the liquid.

It may sometimes be required to find the comparative acidity of two samples of nitrate of iron. For this purpose bring both to the same specific gravity, by adding water to the stronger, and noting the quantity required. Equal measures of the two samples are then taken, and into each of them a standard solution of carbonate of soda is run from a burette, stirring after each drop, till the exact point is reached, when the liquid is neutral to litmuspaper. The number of degrees consumed in each case gives the respective acidity of the samples.

But in the most important points—namely, the purity, brightness, permanence, and evenness of the shades produced—the only method to decide on the quality of a sample of nitrate of iron is to dye with it on a small scale.

In order to test "blue iron" equal measures of each sample are diluted respectively with equal quantities—about five or six times their own bulk—of cold distilled water. Equal weights of clean calico or of cotton-yarn are then allowed to soak in each sample for an equal length of time. The swatches are then taken out and allowed to drain. Meantime, equal measures of a solution of prussiate of potash, diluted with equal quantities of water, are placed in a number of glasses of suitable size, and in these the swatches are respectively steeped for an equal length of time. They are then taken out, rinsed in cold water, dried, and compared.

"Black irons" are tried by taking a number of equal swatches of clean calico, and steeping the whole of them in a solution or decoction of some astringent—such as galls, myrobalans, sumac, &c.—for one hour. They are taken out and allowed to drain, and are then placed respectively in the different samples of nitrate of iron, two fluid drachms of each being diluted for this purpose with half a pint of cold water. After soaking for ten minutes the swatches are taken out, rinsed in cold water, dried, and compared.

For testing "common irons," swatches treated as above are steeped in a weak solution of alum. That which is least affected by this treatment is preferred.

The following iron mordant is recommended by some dyers as safe and useful:—Dissolve 78 lbs. red oxide of iron in 117 lbs. sulphuric acid. Dilute with water, and add 17 lbs. of sulphate of potash, and allow the compound to

crystallise. It gives results very similar to those produced by the nitrates of iron made from copperas.

Alkaline Iron Mordants.

Certain compounds of iron are soluble in alkalies, and may be used as mordants:-

1. Take a very neutral persulphate of iron, dissolve it in water, and precipitate it with the phosphate of soda. The precipitate—a white powder—can be dissolved in ammonia, and constitutes the mordant in question. According to Persoz, a madder-bath, spent as far as the ordinary mordants are concerned, will still dye goods mordanted with this preparation.

2. A concentrated solution, either of metallic iron or of copperas in nitric acid, is mixed with a strong solution of carbonate of potash. The precipitate which first forms re-dissolves in an excess of the alkaline liquid, forming a red solution.

Lead Mordants.

Though several compounds of lead are used in dyeing and printing, this metal can scarcely be said to give rise to true mordants. The acetate (sugar of lead) and still more the sub-acetate (basic acetate) have a great affinity for colouring matters, and when the latter is added to the solutions of dyewares everything dissolved is generally precipitated, and the supernatant liquid left colourless. These lakes are, however, of little value, being void of depth and brilliance. This arises from the fact that a great variety of other substances besides the tinctorial principles are also precipitated. Hence the lead-lakes are not articles of commerce, and are not employed in pigment styles. The affinity of lead for vegetable fibres is not great, and the liability of all colours of which it forms a constituent to become blackened, or at least darkened, on exposure to sulphuretted hydrogen is a serious obstacle to its use. It is not a good mordant for wool, where it is liable to injury from the presence of sulphur. In 1859 Messrs. Perkin and Gray patented a process for fixing the aniline purple or mauve by means of a lead mordant. In dyeing, the goods are worked alternately in solution of acetate of lead and in ammonia, and then dyed in the ordinary manner. In printing, acetate of lead is applied to the cloth, and fixed by means of a mixture of soda crystals and ammonia. The process is not now in common use.

Nitrate of Lead is formed by dissolving litharge in nitric acid with the aid of heat, and allowing the solution to crystallise. It forms large white crystals, readily soluble in water. It is used in mixing murexide purple, and, like the acetate in forming chromate of lead in cotton goods, along with the chromates of potash.

Sulphate of Lead, although insoluble in water, has the property of attaching itself to vegetable fibre, and can thus serve as a preparation for chrome yellows and oranges.

Alkaline Solutions of Lead.

Lead is also capable of playing the part of an acid and combining with alkalies. The plumbite of soda is formed by dissolving litharge in caustic soda as long as anything is taken up. The resulting liquid must be preserved, as far as possible, from contact with air. The plumbate of soda is formed in

a similar manner, red-lead being substituted for litharge. Both the plumbite and the plumbate deposit a certain amount of lead upon vegetable fibres, and can be used in getting up chrome-yellows. Their affinity for organic colouring matters is too feeble to admit of them serving for purposes similar to the stannates.

Tungsten Mordants.

Tungsten, or wolfram, is a metal which is frequently found along with tin, and which has been tried as a mordant in various states of combination. The use of certain tungstic salts in dyeing was patented, in 1847, by Robert Oxland. He directs a chloride of tungsten to be made by boiling tungstate of soda with nitro-hydrochloric acid, and to be used in cloth-dyeing in place of the salts of tin. The shades produced upon wool with logwood are violet, passing on prolonged boiling into claret, and finally into black. He prepares the tungstate of soda by roasting the ore, either native wolfram (the double tungstate of iron and manganese)or "native tungstic acid," with soda-ash, or sulphate of soda. As prepared under this patent, the tungstate of soda would require to be freed from admixtures of ferrate and manganete.

Haeffely, in a patent dated 1854, claims the use of this tungstate of soda either as a substitute for, or as an addition to, the stannate of soda.

The general conclusion, among printers who have given the tungstate a fair trial, is unfavourable.

Antimony Mordants.

Antimony, like bismuth, has a considerable analogy with tin. When acted upon by strong nitric acid it—like tin—forms an insoluble oxide, and its acid solutions, like those of bismuth and tin, are rendered turbid and precipitated if largely diluted with water,—a reaction which may be prevented by the addition of tartaric acid.

The tartrate of antimony, the double tartrate of antimony and potassa,—commonly known as tartar emetic,—the chloride and the double oxalate of antimony and potassa, and the alkaline antimoniates, have been made the subjects of various experiments in dyeing and printing. The results, though they do not preclude all hope of success in the future, have not been satisfactory.

Solutions of antimony along with oxalic acid have been tried for cochinealscarlets in place of the corresponding tin preparations. The result was a coarse harsh shade, without the richness and softness of the tin cochineal-scarlet. As "prepares" for steam-colours, all the antimonial compounds hitherto tried have shown themselves inferior to tin.

Jones Martyn Roberts, in 1853, patented the use of antimony, "rendered soluble in any form," as a mordant. He also claims its use as a "brightener." It is remarkable that several antimonial compounds, if digested in very small quantity with logwood liquor, modify its colour to a rich rose-purple, almost approaching certain aniline colours. The logwood so modified gives, however, only weak stains upon fibres and tissues.

Antimonial compounds have been used in the preparation of aniline colours, and the double tartrate (tartar emetic) serves as a mordant for fixing colours of this class upon cotton.

Solutions of antimony yield readily, with solutions and decoctions of dyewares, a series of lakes, many of which, if the antimony is free from iron, are eminently beautiful. This property of antimony, which was then no novelty, was claimed by F. A. Gatty, in a patent obtained in 1856. He applies the salts of antimony, preferably the chloride, for the purpose of precipitating the colouring matters of dye-materials, such as sapan wood, logwood, cochineal, quercitron, &c., thereby producing colours called lakes, for the manufacture of which other metallic salts have hitherto been used. To I gallon of chloride of antimony, of 80° Tw., he adds 20 gallons of well-aged sapan or Lima-wood liquor, at 7° Tw.; the whole is then well stirred and left to stand for a few hours, and then is put on a filter. When the liquor has run off he adds 4 gallons of water to wash the precipitate. The washing is repeated a second time. When the water is drained off the lake is finished, and may either be dried or used in the wet state. The shade of the lake may be varied from a crimson to more of a scarlet, by using more or less of the chloride. For "purple or violet lakes" logwood is substituted for the sapan wood, and bark-liquer for yellows.

The practical difficulty in this process is that the chloride of antimony is precipitated by water alone as decidedly as by solutions of colouring matters. Hence it follows that, in addition to the true antimonial lake, a variable quantity of antimonic oxychloride (salt of algaroth) is thrown down, which dilutes and "flattens" the colour of the lake. To prevent this an addition of tartaric acid would be necessary, previous to mixing the antimony solution with the sapan liquor.

Bismuth Mordants.

Bismuth presents certain analogies with tin, which have led to the opinion that it might be valuable as a mordant. It possesses a strong affinity for colouring matters, and with proper precautions it gives rise to a variety of beautiful lakes. On the other hand, its affinity for animal and vegetable fibres is less decided than that of tin. Its acid solutions, on dilution with water, are decomposed too readily, the bulk of the bismuth being thrown down, in the state of an insoluble sub-salt, without the application of heat, and without the presence of any organic fibre or tissue. This evil can be to some extent prevented by the addition of acetic acid, but the shades produced, as far as our present experience goes, though rich and brilliant, are deficient in evenness and solidity.

In 1855 E. Kopp took out an English patent for the use of the aceto-nitrate of bismuth as a "mordant for garancin colours." This salt was to be prepared by dissolving as much bismuth as possible in hot nitric acid (strength and temperature not stated), diluted with half its weight of water. On cooling, yellowish crystals are deposited, which, dissolved in acetic acid at 8° Tw., constitute the improved mordant. According to the inventor, this aceto-nitrate of bismuth gives, with garancin, peculiar bright crimsons, and, when mixed with a solution of arseniate of iron in nitric acid, it produces, with the same dye-ware, peculiar dark crimson and purple-crimson shades. Prior to this date all the easily-prepared preparations of bismuth had been tried in England, by C. O'Neill and others, without any valuable results. The specification above quoted, after careful and repeated trials, yielded nothing of any commercial value. Mr. O'Neill, who had an opportunity of examining the patentees' original patterns, pronounces them no better than those obtained in this country.

Bismuth has two additional disadvantages as compared with tin: its price is very considerably higher, and it is more liable to be blackened by sulphuretted hydrogen in the atmosphere.

Chromium Mordants.

A variety of chromium compounds have a very decided action both upon organic fibres and upon colouring matters. The most important of these is chromic acid, which is always used in combination with potash. The bichromate of potassa, commonly known as bichrome or red chrome, is a salt too generally known to require any description. Pew commercial chemicals are more generally met with in a state of purity, and it is, we believe, never intentionally sophisticated. It should show no whitish or yellowish spots or incrustations. It should be perfectly soluble in pure water, leaving no sediment or turbidity. If a little nitric acid is added to the aqueous solution of bichrome, a solution of nitrate of baryta should not occasion any precipitate. If one appears, sulphuric acid is present, in the state of sulphate of potassa.

The neutral or yellow chromate of potash is comparatively little used. Its action is milder, and more easily regulated than that of the red chromate, and with organic colouring matters it yields a variety of interesting results, many of which require and deserve further investigation. Against the above-mentioned advantage must be set the fact that it is exceedingly variable in composition, two samples being rarely found quite identical. The results are hence uncertain. Those who wish to experiment upon its action on a practical scale can employ a solution of 151 parts of bichrome and 143 parts of clean

crystallised carbonate of soda, not effloresced.

The principal use of red chrome is to produce blacks upon wool, along with logwood, smaller quantities of other wares being added to modify the shade. Chrome-blacks are cheap, both from the low price of the materials and from the small amount of time and labour required. The shades produced are, however, inferior both in beauty and permanence to the old logwood and copperas black.

With other dye-wares red chrome produces a variety of browns, yellowbrowns, yellows, oranges, bottle-greens, olives, black-greens, and purples. The action of the chromes upon logwood is exhaustively treated in Dr. Runge's

work, "Farben-Chemie," Part III.

Chromic oxide, in combination with acids, is also a mordant, though little used. The most important of its compounds are the sulphate and the nitrate. It has the disadvantage of imparting, in itself, a pale greenish colour, which to certain shades would of course be fatal. Its affinity, for many colours at least, is but feeble, and many dyers complain that the shades produced are harsh and dull.

Chrome-alum, a double sulphate of chromic oxide and of potash, is occasionally employed on the Continent. The salts of chromic oxide may be used to fix aniline blues upon cotton.

From the immense use of bichrome in dyeing it is very possible that certain quantities of this powerful poison may find their way into rivers. In all sanitary legislation its exclusion, even in minute traces, should be rigorously insisted on.

Manganese Mordants.

Manganese has a very powerful affinity for organic fibre, both animal and vegetable. This is most strikingly shown with the solutions of permanganate of potash. If a slip of calico is plunged into such a liquid it rapidly takes a deep brown colour, permanent as far as light is concerned, but not capable of resisting treatment with acids. The intensity of the colour thus produced would disqualify it as a mordant, except for some of the darkest shades. As the compound of manganese thus fixed upon the fibre is a hydrated peroxide, and as the protoxide is white, or exhibits at most a faint pinkish tinge, it may be used as a mordant by bringing a powerful deoxidising agent to act upon it either along with or immediately before the colouring matter.

The use of the sulphate and chloride of manganese in producing certain so-called bronze effects upon cotton, independent of any organic colouring matter, is not a case of mordant action, and is, moreover, nearly obsolete.

Zinc Mordants.

The affinity of oxide of zinc for organic fibres is very feeble. With the majority of colouring matters, also, it shows little disposition to form lakes. Hence its uses as a mordant are unimportant. Some experimentalists have obtained a scarlet from sandal wood with a mordant of chloride of zinc. With murexide salts of zinc produce a yellow, which, though good, has no distinctive feature to recommend it in preference to similar shades more cheaply producible. Chloride of zinc, on account of its deliquescent nature, is sometimes added to printers' colours with the object of preventing the mixture from drying up. It is also employed to fix the alumina of "alkaline pink mordant" upon the fibre. Certain manufacturers of mordants maintain that if a solution of zinc-nitrate, chloride, or sulphate as the case may beis added to a tin spirit, it causes the tin to be thrown better upon the fibre, and by being thus more thoroughly utilised it enables a smaller quantity to answer the same purpose. We know of no facts to substantiate this hypothesis, which we are inclined to suspect may have been devised to justify what was at one time a not uncommon mode of adulterating the preparations of tin, and is probably not yet extinct. The action of chloride of zinc upon alkaline pink mordant, as above mentioned, depends obviously upon a principle which cannot apply here.

Arsenic Mordants.

Arsenious acid occurs in a great number of printing receipts, its function being often very doubtful. In some cases it plays the part of an alterant rather than of a true mordant. Arsenite of soda mixed with the acetate of alumina is employed as a mordant for printing aniline colours upon cotton. Arsenious acid, boiled with decoctions of the woods, fixes a variety of browns upon cotton and woollens, which are, however, more curious than practically important. The poisonous nature of the arsenical compounds undoubtedly tends to restrict their tinctorial applications.

Copper Mordants.

Certain preparations of copper are rather extensively used in dyeing and printing, although their function is less that of mordants, strictly so-called, than of alterants, or oxidising agents.

Acetate of copper, commonly known as verdigris, occurs in commerce in several varieties. The common blue verdigris is a bibasic salt, forming delicate, loose, blue scales and needles, which yield a blue powder. It consists of 2(CuO,C₄H₃CuO₄). It is prepared by packing wine-lees loosely in casks, with straw, till the acetous fermentation sets in. When that is ended they are arranged in pots covered with straw in alternate layers, with alternate layers of copper plates heated to the temperature of 40° C. These plates when used for the first time are previously moistened with a solution of the neutral acetate of copper and dried. At the end of about three weeks the plates are withdrawn, set upright to dry, dipped six or eight times in water in the course of as many weeks, and again left to dry, during which operation the verdigris continually swells up. It is then scraped off, and the plates are again replaced alternately with fresh acid wine-lees, and the same operations are repeated till the copper is corroded away.

Common green verdigris is a mixture of the sesqui-basic acetate of copper, with small but variable quantities of the bibasic and terbasic salts. It is prepared by repeatedly sprinkling copper plates with vinegar in a warm room.

In calico printing acetate of copper is used in solution, and is prepared by the double decomposition of sulphate of copper and sugar of lead. The following mixture is often employed:—I gallon of water at 160° F.; 4 lbs. white sugar of lead; 4 lbs. sulphate of copper. The ingredients are previously ground up, and the mixture is frequently stirred till the decomposition is complete, when the sulphate of lead is allowed to deposit, and the clear liquid is drawn off. The respective proportions of sulphate of copper and of sugar of lead are varied in different establishments, some using 2 lbs. only, and others as much as 6 lbs. of sugar of lead to 4 lbs. of sulphate of copper. It is obvious that where the smaller proportions of sugar of lead are used, the resulting solution must contain a considerable quantity of sulphate of copper mixed with the acetate.

The uses of verdigris are less extensive than was formerly the case. It is used in many catechu colours, in certain resists for indigo blues, and as an oxidising agent in a few steam colours. In black dyes for silks and for hats, and for printing blacks on silk goods, verdigris is also employed. Logwood blues on wool are also dyed with an admixture of a salt of copper, generally verdigris. The A& George III., 20, which imposes a penalty of £20 for every piece of cloth dyed blue by means of this process, is a curious specimen of the commercial legislation of our forefathers, and is supposed to be still unrepealed. Verdigris figures in a great variety of old dyeing receipts where its utility is exceedingly doubtful, or rather where its inutility has been satisfactorily demonstrated.

Ammoniuret of Copper.—On adding ammonia to solutions of the sulphate, nitrate, or other salts of copper, a pale bluish-green precipitate is thrown down, which, on the addition of a larger quantity of ammonia, re-dissolves, forming a solution of an intense violet-blue. Cotton, steeped in this solution, swells up, becomes a jelly, and is finally liquefied. On the addition of an acid, however, the cotton is re-precipitated as a white powder, chemically unaltered, but having its fibrous structure destroyed. Dilute solutions of the ammoniacal copper compound may be used for dyeing a pale green, by padding, drying, and finally washing.

Chloride or Muriate of Copper.—This compound is best made by the double decomposition of a mixture of chloride of calcium and sulphate of copper in hot water, the whole, after the solution of the ingredients and after thorough stirring, being left to settle, and the clear liquid drawn off for use. It is much used on the Continent, but in English dye- and print-works it is generally replaced by the sulphate, or the nitrate used along with sal-ammoniac.

Nitrate of Copper.-This salt is sold both in the form of crystals and in solution. It may be easily prepared either by dissolving copper clippings and turnings in nitric acid to decided saturation, or else by a process of double decomposition. For this purpose a saturated solution of sulphate of copper is mixed with a solution of the nitrate of lime, or, better, the nitrate of lead, in equivalent quantities. The solution thus obtained is perfectly neutral, and may be concentrated to any strength required. The nitrate of copper, whether in the crystal or in solution, is of a deeper and less green shade than the sulphate. It is less generally met with in the solid state, as it is very deliquescent, and attracts moisture from the atmosphere. In solution it is generally sold at from 80° to 100° Tw. Those who judge of its quality merely by means of the hydrometer often find themselves mistaken, as it is not unfrequently contaminated with zinc and other bodies. The presence of such foreign matters will be easily understood if we remember that nitrate of copper is now generally made, not by the dyers or printers themselves, nor by manufacturing chemists whose speciality it is to prepare tinctorial requisites, but by workers in metals. These parties use nitric acid to a considerable extent in cleansing articles of copper and its alloys, &c. The resultant liquids, mixed promiscuously and concentrated, are sold at a very cheap rate. Such samples of nitrate of copper, beside containing foreign metals, may be too acid, and may then prove very injurious. The comparative acidity of different samples may be judged by noting the relative amounts of caustic soda solution of uniform strength which are required to produce a permanent precipitate, i.e., one which will not disappear on agitation. If an excess of ammonia is added to the nitrate of copper, the precipitate formed at first should entirely re-dissolve. If anything remains undissolved, iron or lead is probably present. If a portion of the nitrate of copper is mixed with a little pure hydrochloric acid, and a current of sulphuretted hydrogen passed through it until it is completely saturated, the precipitate produced should contain the whole of the fixed matter present. If it, therefore, be filtered off, the clear filtrate, on evaporation to dryness and raising to very low redness, should leave nothing. Any permanent residue is probably due to the presence of zinc, a frequent, though for the most part an unintentional, impurity.

Sulphate of Copper, known also as Blue Stone, Blue Vitriol, and Roman Vitriol, is now generally prepared on the large scale direct from the ores. It forms large, hard, deep blue crystals, soluble in 3 parts of cold and in ½ part of boiling water. In a dry atmosphere the crystals are apt to effloresce, losing part of the 36 per cent of water normally present. A solution of blue vitriol saturated at 62° F. stands at 36° Tw. If the crystals are exposed for some little time to a temperature slightly exceeding that of boiling water, the water of crystallisation is expelled, and there remains the anhydrous sulphate in the form of a white powder. In contact with minute traces of water this powder resumes its blue colour, and may, therefore, serve to detect the presence of

water in alcohol, etler, &c. At full redness the sulphate of copper is decomposed, the oxide of copper remaining in the form of a black powder.

Sulphate of copper is often found to be impure. The protosulphate of iron (copperas) is capable of crystallising along with blue vitriol, in a very considerable proportion, without any alteration in its form and colour. To detect the presence of iron the solution is boiled with a little nitric acid, and an excess of ammonia is then added. If any iron is present, brown flocks will remain floating in the ammoniacal solution of copper. Zinc may be detected, along with manganese, magnesia, &c., by the process with sulphuretted hydrogen, as described under Nitrate of Copper. The sulphate of copper is used in resists for indigo-blues.

Copper salts have, within the last few years, met with a new application in dyeing and printing aniline blacks, the sulphide being preferred by many.

The presence of copper, where not specially required, should be carefully avoided, as its action is generally injurious, and even in minute traces it is capable of modifying shades in an unexpected and puzzling manner. With madder it proves completely fatal, even in very small quantities. A piece of sulphate of copper put into an indigo-vat throws it out of order, by oxidising the white indigo and sending it—in an insoluble state—to the bottom. This is a method of "rattening," not unknown in dye-works.

Tartar and Argols.

These substances, though not mordants, require a brief notice in addition to the remarks made on p. 112. They occur in commerce in three principal states,-white argol, red argol, and tartar. Good white argol is met with in flattish pieces, having on one side a distinctly crystalline texture, and on the other showing traces of the fibre of the wooden vessel in which it has been allowed to crystallise. If a piece is broken the fracture should look bright and crystalline, and the bits, if shaken together in the hand, should ring like fragments of pots. Argol should melt slowly in the mouth with a pleasantly acid, but not vinous taste. The powder should be white, faintly bordering upon pink or pinkish-grey. On the addition of dilute nitric acid no effervescence should be perceptible. An escape of gas shows the presence of carbonates, either of lime or of the alkalies. If a weighed portion of the sample is digested in dilute nitric acid, until everything soluble has been taken up, sand and organic matter will remain, and may be filtered off. When washed, dried, and weighed, it should not exceed 2 per cent, though in adulterated samples it may reach 15 or 16. The dregs of white wines are now a common sophistication. On drying they form small grey or reddish lumps, or clots, less brittle than argol, and without a trace of crystalline structure. This matter differs also in taste from argol, being very faintly acid.

The solution filtered from the organic matter and sand may be examined for other impurities. If the addition of a solution of chloride of barium produces a white turbidity or precipitate, sulphuric acid is present, showing the probable existence of an alkaline sulphate (sulphate of soda) or of alum as a sophistication. It must, however, be remarked that the juice of the grape contains a certain small amount of sulphate of potash. If the precipitate given by chloride of barium, however, is abundant, the sample cannot be genuine.

Another portion of the solution may be mixed with a solution of nitrate of silver. A white curdy precipitate indicates the presence of a chloride, probably common salt.

A third portion of the nitric acid solution of the sample is mixed with ammonia, and oxalate of ammonia is added. If, on stirring the mixture and allowing it to stand for a few minutes, a white precipitate is produced, lime is present. A small amount of lime is of course naturally present, due to tartrate of lime. If the precipitate produced is plentiful, sulphate or carbonate of lime has been added.

Red argols are less frequently sophisticated. Both these compounds are extensively used in dyeing; the white kind for scarlets, crimsons, and other grain-colours; red argol is used for certain blacks and other dark shades.

White argol, dissolved, filtered, and re-crystallised, is known as grey tartar, and on still further purification it becomes white tartar. The tartars are used in dyeing pinks, maizes, &c.

Liquid tartar, otherwise known as protartar spirits, is prepared as follows:-

Mix-Grey tartar or white argol	 	 	to lbs.
Sulphate of soda, crystals	 	 	10 ,,
Dilute sulphuric acid, at 90° Tw.	 	 	6 quarts.

Then add water sufficient to let down the whole to 17° Tw. This liquid is employed by some dyers for "levelling" certain colours, especially aniline blues, upon woollen and worsted goods.

Tartaric Acid, obtained by the decomposition of the tartrates, is extensively used both in dyeing and printing. Sometimes it is sophisticated with bisulphate of potash. To detect this fraud a small quantity of the sample is heated to redness upon a slip of platinum foil, or in a small platinum capsule. If bisulphate of potash is present a white fused mass will remain, but if the sample is genuine nothing will be left. Tartaric acid is sometimes used in grain-dyeing. In printing it serves for a discharge on Turkey reds and dip blues, and in steam greens and blues it is used to decompose the yellow prussiate of potash.

A solution of tartaric acid in water is sometimes sold under the curious name of "essence of tartar." Not unfrequently this "essence" is weighted with sulphuric acid, which may be detected by acidifying with pure hydrochloric acid, and adding chloride of barium in solution. A white precipitate shows the presence of sulphuric acid, added either as such or as a sulphate.

Since the grape-disease first made its appearance, and since the accompanying rise in the price of argols, tartars, and tartaric acid, a number of compounds have appeared in the market under such names as tartar substitutes, pro-argols, pro-tartars, &c. These bodies profess either to economise or totally to replace the real substances. Some of these contain argol or tartar in various proportions; others are mere mixtures of common salt, oxalic, acetic, and sulphuric acids, alum, &c. These substitutes may in some cases prove satisfactory. Certain dyers, for instance, are in the habit of using argol, where nearly any acid would answer the end required. In such instances the substitutes may give satisfaction. But where the distinctive properties of the bitartrate of potash are really needed, these pro-argols can only lead to disappointment. Some makers, however, prudently recommend that a certain

amount of genuine argol or tartar should be used along with the substitute. One of these compounds, the so-called "tartar cake," is made by mixing sulphate of soda with some free sulphuric acid and a small quantity of white argol or tartar. The mixture is melted, run into thin layers, and broken up when cold. It is deliquescent, corrosive, and intensely sour. In stuff-dyeing it is used for the so-called sour browns.

Super-Argol is white argol to which sulphuric acid has been added, enough to combine with all the potash present. It is, therefore, a mixture of

sulphate of potash and of free tartaric acid.

The following is a mixture, patented by B. Barcroft, as a substitute for tartaric acid "in the production of blues and in the reduction of pinks in dyeing and printing:"—Mix 14 quarts of sulphuric acid, at 170° Tw., with 12 quarts of cold water, and allow it to stand till cool. The inventor then "takes a large vessel and places it in a water-bath, and pours into it 20 quarts of boiling water, and adds 48 lbs. sal-ammoniac and 6 lbs. of white arsenic," boiling till all is dissolved. The solution is then cooled down to 70° F. The first mixture (dilute sulphuric acid) is then added, and the whole allowed to stand till quite cold: 3 quarts of oxymuriate of tin, of 120° Tw., are then added, and in a few days it will be ready for use.

A. E. L. Bellford attempts to prepare, from the reaction of sugar and nitric acid, a body less highly oxidised than oxalic acid. Gatty patented the use of lactic acid as a substitute for tartaric. These preparations, however, have never come into general use, and are probably now completely abandoned.

Royal Blue Spirits.

Under this name is known a mixture of acids, used in dyeing Prussian blues upon wool, for the purpose of decomposing the prussiate of potash. It contains neither tin nor any other base. Where the yellow prussiate is employed the following mixture is given as one in actual use:—

Some dyers prefer to diminish the latter ingredient by one-half. The whole of the acids are well mixed together, carefully avoiding the fumes.

If the red prussiate of potash is used, the nitric acid (aquafortis) is omitted altogether.

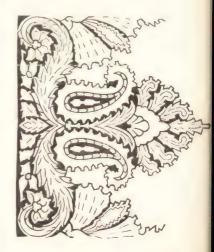




"Gas-process" for Engraving Blocks for Printing.

The graving-tool is heated to redness by means of a small gas-burner, and destroys all parts of the surface except those to be left in relief.





DESIGNS PRODUCED BY THE "GAS-PROCESS."

CHAPTER VIII.

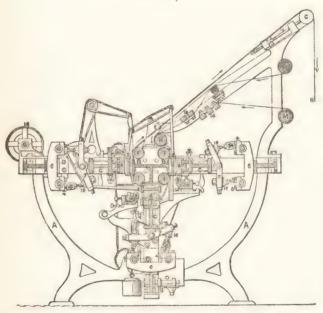
PRINTING.

BEFORE proceeding to give a systematic description of the various styles of printing, a brief account will be required of the two principal machines used in modern print-works,—the perrotine and the cylinder machine. The former of these executes a style of work very similar to hand-block printing. Three wooden blocks, from 21 to 3 feet in length, according to the width of the pieces, and varying in breadth from 2 to 5 inches, have the pattern engraved in relief on their surface. They are fixed, with their faces at right angles to each other, in a stout iron frame, and can each in turn be brought down upon the front, top, and back, of a four-sided iron prism, faced with cloth, and revolving upon an axis. The goods to be printed pass between the prism and the pattern-blocks, and receive the impressions in succession. The blocks are forced down upon the calico by means of springs, so as to imitate the pressure of the hand of the block-printer. After each impression the block takes up a fresh coat of colour, by contact with a surface of flannel, upon which the mixture is kept continually applied by means of a self-acting brush. The perrotine is shown in section in Fig. 24, and in elevation in Fig. 25, both these illustrations being taken from the "Traité de l'Impression des Tissus" of Persoz.

A, cast-iron frame. BBB, cast-iron tables, planed smooth, over which pass the blanket, the back-cloth, and the calico to be printed. ccc, sliding pieces, on which are screwed the block-holders, 3, causing the pattern-blocks, 2, to move in turn against the layer of flannel and the pieces to be printed, by means of the play of the levers 4 and 5, whose supports, 6, rest upon A, and act, by means of coupling-rods, upon the beams, 7, keyed to the slides c. The lower of these sliding-pieces is vertical, and takes by its own weight a retrograde movement, regulated by a counter-weight. EEE are movable coloursieves, fixed to coupling-rods, and receiving a suitable movement from the power which works the machine. The sieves are flat, and covered with cloth on the face opposite to the block. They work in grooves on the sides of the tables, and receive from the furnishing rollers the colours, which they then pass on to the pattern-blocks. FFF are colour-troughs, filled with the colour mixture, and fitted each with two rollers, 8 and 10. The latter dips into the trough, takes up colour, and transfers it to 8, which is covered with woollen cloth, and which it carries on to the sieves, E, where it is spread by the brushes, 9. In order to regulate the amount of colour supplied to the sieves, and thence to the blocks, the rollers, 10, are fitted with levers, 11, which, by

means of set-screws, bring them into more or less close contact with the other rollers, 8. Thus the amount of colour taken up can be varied at will. The revolution of the blanket, back-cloth, and pieces is regulated by the following contrivance:—At the angles of the three tables B are rollers, I, their surfaces being fitted with needle-points. These prevent the cloth from slipping as it passes round, and cause the pieces to be printed to move on regularly. This movement is effected by the cog-wheels, 2I (Fig. 25), keyed on the ends of the axles of these rollers. G is a roller which stretches the endless web, resting with the ends of its axles on two cushions forming the ends of the screws, I2. By these the roller, if needful, can be pushed further out, so as to stretch the cloth to the degree required. H is another stretching-roller, which supports the blanket and back-cloth. K is another roller, which serves to stretch the

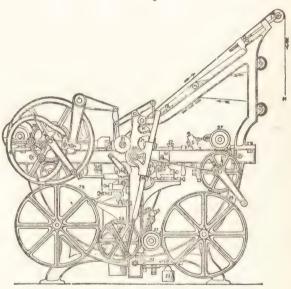
FIG. 24.



blanket, back-cloth, and pieces. T is the blanket, passing round the semicircumference of the roller G, over H and behind K, round I, and over the surface of the tables B. L is a cylinder from which the back-cloth is unwound, having been first stretched by H, and smoothed by the scrimping-bars, I3. It then joins the blanket at the roller K. M is a roller from which the piece to be printed is uncoiled by the revolution of the machine, passing over the scrimping-bars, I4, and joining the blanket and back-cloth at the roller K. It accompanies the two latter till it arrives at G, when it is led off towards N, and is dried on the hanging-rollers. The whole machine is moved either by hand, with a winch, or by steam-power, when a driving band is passed over the pulley 18, arranged with different diameters, so as to give different degrees of speed. It carries catches, locking into a sliding catch-box on the shaft

when the machine is set in motion. The movement of the machine is necessarily intermittent, and is regulated so that the piece moves on a space exactly equal to the breadth of the block, and moves forward while the sieves are supplied with colour from the rollers, 8, 8. This arrangement is produced by means of a dividing-wheel, 20. The wheels 21, keyed on the axle of the cylinder 1, and having each the same number of teeth, are moved by a central wheel with teeth in the same manner, and fixed behind the wheel 20. The latter receives an alternating movement from a rack, 24, fixed in a copper piece, 25. This rises and falls alternately, and is keyed at its lower end to one of the spokes of the wheel 28. By altering the point of attachment to the spoke the range of its movement is varied, more or fewer of the teeth of the wheel are allowed to pass, and the advance of the piece at each movement





is proportionately increased or lessened. It is further regulated by the ratchet-wheel, D. At each half-revolution the lever 22 raises the catch, and throws the wheels 21 out of gear during the next half turn; but as in working these wheels there would necessarily be a backward movement, this is prevented by a break, which consists of a pulley fixed on the shaft of the axle of the wheel 20, and a wire, which, after making a turn and a half or two turns on this shaft, is stretched by the weight 23, which offers a sufficient resistance to any recoil. The slides are moved by the wheels 27 and 28 gearing with the larger wheel 29. In order to regulate both the pressure and the amount of colour, the points of junction, 16 and 17, are moved to a greater or less distance from the point 15. The movement of the sieves is regulated by the cam, 11, 30, which moves them by means of a shaft to which they are keyed.

The furnishing-rollers are moved by gearing with pinions on the axes of the rollers 8, 8.

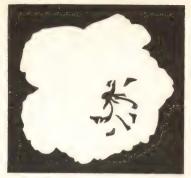
The working of the perrotine may be described as follows:-The piece moves on a length equal to the breadth of the pattern-blocks, along with the blanket and back-cloth. The portion of the piece which issues from the third block is fully printed; what was under the second advances under the third; what was under the first moves to the second, whilst a fresh portion of white calico comes up to the first. While the calico is thus moving the sieves take the place which they hold in Fig. 24; the first on the right hand rises, the second moves from left to right, and the third is lowered. All three press on the furnishing-rollers, 8, where they take up the colour which has been spread evenly by the brushes, g. Meantime the sliding block-holders move forward, and push the blocks against the sieves, so as to furnish them with colour. At the same time the slides give the blocks a gentle movement backwards, while the sieves deviate from their position. The blocks then return, and are drawn back after having been pressed to a fresh part of the colour surface. When these movements have simultaneously taken place the action proceeds, the colour-sieves move back from before the blocks, and these are pushed up against the latter, and print that part of the calico which is stretched upon them. The machine is now again at the point at which the description began.

The perrotine, as will be plain from the above description, is adapted for patterns containing three distinct colours. It is extensively used in France and Belgium, one machine doing the work of twenty skilled block-printers. It executes some styles of work which the cylinder machine cannot execute without the aid of the surface-roller.

In England the perrotine is in much less general use than in France. The cylinder-machine, on the contrary, a Scotch invention, has received its chief development in this country, and, except for a few particular styles, has quite displaced hand-printing. One of them, managed by one man, assisted only by two boys who attend to the colour troughs, performs as much work as two hundred men and boys could do with the blocks. In some styles a mile of cloth can be printed hourly by a single machine.

The following diagram gives a general idea of this system of printing (Fig. 26). The design to be printed is engraved on the surface of a hollow copper roller, which is forced by pressure upon a stout mandrel of iron, which serves it for an axle. To aid the transfer of the pattern to the calico to be printed, the pieces are lapped around another large cylinder, which is rendered elastic by a coating of stout woollen cloth. The pattern-roller presses the calico against this elastic cushion, and consequently prints it as it revolves. In the engraving A is the pattern-roller mounted on its mandrel, which receives rotatory power from a wheel at its end, in connection with the steam or water power of the works. B is a large iron drum, turning in bearings of the end. frames of the machine. The pattern-roller, A, is pressed against this drum by weights or screws, the weights acting steadily upon its brass bearings by levers. Round the drum, B, an endless web of felt or blanket travels in the direction of the arrow, and is carried round by the drum, B, which again is turned by the friction of the cylinder, A. c is a wooden roller, covered with cloth, and partly plunged in the colour mixture of the trough, DD. C is

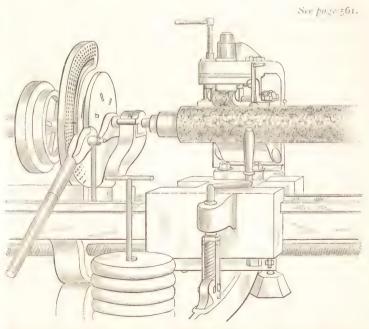








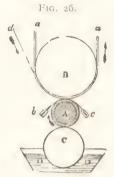
BLOCKS SUCCESSIVELY APPLIED TO PRODUCE THE DIFFERENT SHADES IN A FLOWER.



MACHINE FOR ENGRAVING THE CYLINDERS USED IN "MACHINE-PRINTING."



preferably driven from the cylinder, A, by means of toothed wheels attached to their ends, so that the revolution of c may be more rapid than that of A. Since A is pressed upwards against B, the bearers of the trough and of its roller are attached to the bearings of A, to preserve its contact with c; b is a sharp-edged ruler of gun-metal, steel, or German-silver, called the colourdoctor, screwed between two stiffening bars of gun-metal; the edge of the doctor being slightly pressed at a tangent against the cylinder, A. The doctor vibrates with a slow motion from right to left, so as to exert a delicate shaving action upon the engraved surface as this revolves in the direction shown by the arrow; c is another sharp-edged ruler, the lint-doctor, serving to scrape off any filaments of cotton which may have come off the calico, and, which if allowed to remain on the pattern-cylinder, might either smear the work, or prevent the colour from filling up some of the lines of the engraving. This lint doctor presses very slightly against the cylinder, A, and has no transverse motion. The calico, shown by d, is carried in along with the blanket, a a, in the direction of the arrow, and is passed on by the revolution of A, receiving the pattern engraved upon that cylinder. The object of the colour-doctor is



to remove any excess of the colour mixture. Where a pattern contains more than one colour it requires a compound machine, with a corresponding number of cylinders mounted in one frame. In arranging these machines several adjustments become necessary. It is most important to ensure a correspondence between the parts of the design in the successive printing-cylinders. for unless those of the second and following are accurately inserted in their places and register with the first, the pattern produced on the cloth will become confused. Fig. 27 is the end elevation of a 4-colour machine, and Fig 28 a section. The same letters refer to both. A is the cast-iron frame, bolted to a corresponding frame by the bolts, B, with an interval of 3 to 4 feet between; c is the hollow iron pressure cylinder, about 2 feet in diameter, and between 3 and 4 feet long, according to the width of the cloth to be printed. D are the copper rollers, the width of a piece of cloth; E are wrought-iron mandrels, on which the copper rollers are forced. The mandrel is about 4 inches diameter where the roller fits on, but its journals are of less diameter. The patternroller is made with a projecting piece inside, about 1 inch broad and 1 inch deep, extending all the width of the roller. This so-called "tab" fits in a slot cut in the mandrel, which thus causes it to turn without slipping on the

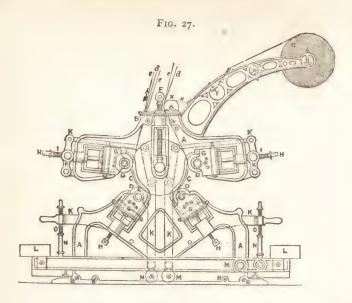
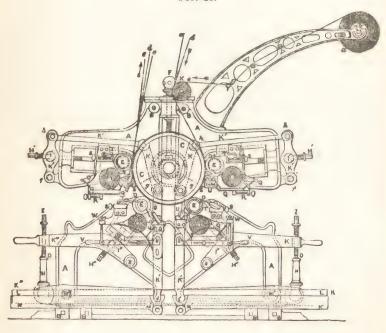
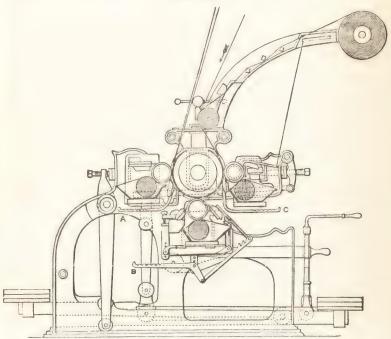


FIG. 28.



mandrel. The pressure cylinder or bowl, c, rests with its gudgeons in bushes, which can be shifted up and down in slots of the side cheeks, A. These bushes are suspended from powerful screws, F, which turn in brass nuts made fast to the frame, A. These screws counteract the upward pressure of the two lowest rollers, and enable the bowl to be lifted out of the way of the rollers when they have to be removed. G G are sliding pieces, moving in arms of the framework by means of screws, H H. These sliding pieces carry the bearings of the mandrels, and to them are also attached the colour troughs and doctors. The screws, H', work in female screws, I', forming part of a system of jointed levers, K. These levers serve to give an additional elastic pressure to the rollers, D. There are four pairs of levers, each bearing upon





one mandrel. The two highest rollers are pressed against the cylinder by the compound levers, κ' , which have attachments to the arms of the framework at f, and to the inside of the main framework at g, and m'' as fulcrums; the screws, m'' m'', working in female screws, m'' m'', as in the other set of levers. For convenience in removing the rollers, colour boxes, &c., these levers are fitted with a hinged piece, m, in a socket, m, on the top of which work the screws, m m0 m1, which by means of the female screw in the lever, m2, serve further to regulate the pressure; the lever, m3, is shown as when the machine is printing, but when the rollers are to be removed the lever is lifted by the handle and the hinged piece, m1, pulled over, the lever with its burden being

then lowered down. The weighting of these levers, which are partly outside the machine, is seen in Figs. 27 and 28. L are weights, o colour boxes, their bottoms and sides made of sheet-copper and the ends of gun-metal; in each end is a slot to receive the brass journals of the wooden furnishing rollers, p, which are lapped with a few layers of coarse calico, and, revolving in the colour and against the pattern-rollers, D, supply them equally all over with the colour; any excess of colour being removed by the doctors, T. These are thin blades of some appropriate metal, often steel, but sometimes German-silver, which are mounted in doctor-shears, that is, plates of metal screwed together with bolts. The shears have journals, which rest in bearings, movable backwards and forwards by the screws, s; the doctors are kept in close contact with the pattern-rollers by levers and weights, for the arrangement of which see Fig. 20, where ABC are the levers attached to the doctor-shears. On the ends of these levers weights are hung, and by this means the doctors are forcibly pressed against the pattern-roller. After printing its pattern on the piece the roller, D, is cleaned from dust or filaments by the lint-doctors, U, pressed against the roller by the screw, s, Fig. 28. The colour boxes are mounted on wooden boards, and tightened up against the roller by the screws, www and RR. The lower pair of colour boxes are removed from the copper roller when not in use by the handles, v, after removing the screws, w w. There is a toothed wheel slipped on to each mandrel, working into a toothed wheel on the axle of the furnishing-roller, which ensures the pattern-roller and furnishing-roller always working together. By an excentric, fixed on the axis of the pressure bowl and connected with each colour doctor, they receive a vibratory movement, which hinders them from being worn down irregularly. Sometimes in machines for more than four colours the colour box is dispensed with, and a doctor placed in a covered frame is applied to the pattern-roller instead. In this arrangement the doctor forms the bottom of the colour receptacle, and is strongly pressed against the roller, the curved frame stopped off at the sides with a piece of copper curved to fit both roller and frame, and which is padded with a piece of folded cotton cloth, forms the colour box. Such a box takes up little room and consumes little colour. The roll of calico is shown at a, wound on the wooden roller, b, the axle of which rests in bearings at the end of the arms. The calico passes under a small wooden roller, next over a square iron bar, and next against the scrimping-bar, y, thence over the wooden roller, a, round which also pass the piece of grey cotton, d, and the woollen blanket, e. The scrimping-bar is made of iron or brass with a curved surface furrowed by grooves, cut right and left from the centre. By passing over this bar the cloth is stretched equally from the centre, and creases are removed. To keep the piece constantly stretched the roller, b, is fitted with a wooden pulley, round which passes a leather strap, one end of which is secured to the framework, and to the other is attached a weight. The friction of the strap against the pulley produces a retarding action, and keeps the piece stretched.

Fig. 30 shows a 12-colour machine, and Fig. 31 a 20-colour, by Messrs. Gadd and Hill, of Manchester.

The surface roller machine executes similar styles of work to those produced by the perrotine. Here the pattern-cylinder is in relief like the hand blocks. Fig. 32 is an 8-colour machine of this class, by Messrs. Gadd and Hill. A A is here the framework; BB the bowl or cylinder, which is hollow,

Fig. 30.

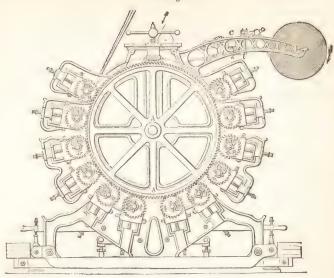
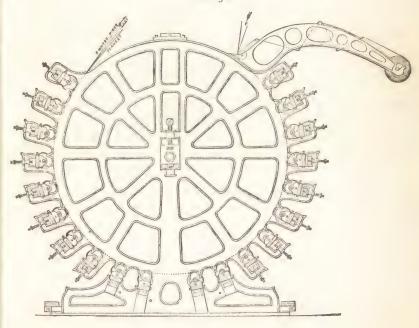
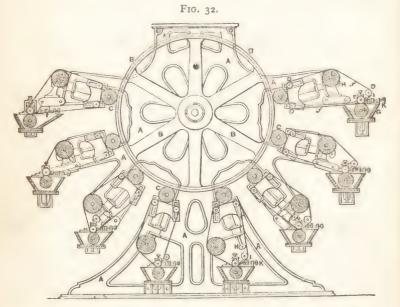


Fig. 31.



and made with arms inside; c c are the surface-rollers supplied with colour by the endless web or sieve, f, revolving round the wooden tension-rollers, d defining roller, e, is screwed down so as to press the sieve on the furnishing-roller, f, which revolves in the copper-colour box, G; the two tension-rollers next to the surface-roller move in slides, so that by means of the screw, H, the sieve can be pressed against the surface-roller; on leaving the furnishing-roller, f, the sieve is wiped by the doctor, i. The printing-roller is in relief, and there is consequently no need for the levers of the common machine. The surface-machine is well adapted for woollen fabrics, and the colours, being laid on the top of the cloth, have a very rich appearance. The outlines are apt to be not well defined.

The general routine of machine-printing is as follows:—The pieces to be printed, generally in lots of forty, are wound on a wooden roller, as shown in



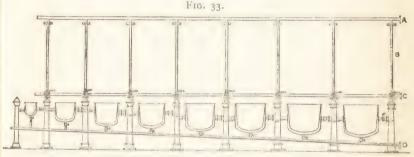
the above engravings. Last of all a few yards of common coarse cotton kept for this purpose are attached. This serves for the printer to fit the pattern on. The printer's assistant stands behind, guiding the cloth evenly, and cutting off any loose threads. The printer stands in front, and, after he has fitted his pattern, attends to the colour boxes, and watches to prevent any irregularity in working. After thirty to forty pieces have been run through, the machine is stopped, the doctors are removed, and the edges are re-touched with the file.

The drum which revolves in contact with the pattern-cylinder is covered first with a coarse, stout cloth, which is wrapped tightly around it to the thickness of \(\frac{1}{2} \) inch. Over this is drawn the blanket, a very important part of the machine. It is a thick woollen tissue, about 40 yards long, very uniform in texture, thickness, and elasticity. One blanket will generally serve during the

printing of 10,000 pieces. A variety of india-rubber blankets have been made and brought into use. Some of these consist of mercerised calico cemented together with caoutchouc. These blankets will serve for 20,000 pieces. Still for certain styles the old woollen blanket is still preferred.

We have not space to enter into a description of the complicated and delicate machinery used in transferring the desired patterns from the flat surface upon which they are first designed to the copper cylinders used in machine printing. The same reason must be given for omitting a notice of the machinery used for running the pieces, after printing, on into the drying room, the machines for stitching together the ends of the pieces to be printed in one roll, the apparatus for freeing the cloth about to be printed from dust and ends of thread, &c.

The colour-house, the place where the ingredients needed in the various operations of a print-works are prepared and mixed, is a large, well-ventilated room on the ground floor. Along one side of it runs a range of colour pans, of various sizes (Fig. 33). These pans are supplied with water, and can be heated or brought to a boil by means of steam. As a rule they turn on pivots, so that they may be the more easily emptied out and cleaned. The range

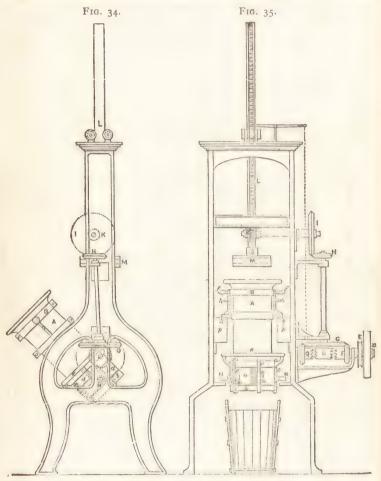


shown in the figure consists of a suit of eight pans, each fitted with a steam-jacket. They vary in size from r to 28 gallons. A is a pipe of copper, closed at one end, and open at the other for the entrance of the steam, which descends through the vertical pipe, B, as far as the stuffing box, e, through which it passes into the steam-jacket of the pan, and escapes by the wastepipe, D. Each pan is fitted with a similar steam-pipe, which can be separately opened or shut off by means of a tap. c is a horizontal pipe, by means of which cold water can be supplied to each pan for cooling. The waste-pipe has steam-tight connections to fit the taps fixed at the bottom of each pan. These can be unscrewed when it is necessary to incline or to invert the pan, and afterwards re-adjusted.

The ingredients for any colour required are placed in one of these pans, and constantly stirred all the time that they are being boiled and incorporated. This operation, which is essential to the production of a good colour, was generally performed by boys called "gum-sticks." Now the colour pans are frequently fitted up with mechanical agitators. When all the ingredients necessary to form a colour have been dissolved and thoroughly incorporated, the steam is cut off, and cold water admitted into the steam-jacket to cool the

mixtures. The pan is then emptied, and the colour carefully strained into a suitable tub or bowl. The object of straining is to remove all gritty particles introduced by any of the materials, which would have a very injurious effect if suffered to remain.

A straining machine, invented and patented by Dollfus and Mieg, has been introduced into this country, and is used with success. It is represented in



Figs. 34 and 35, the former giving the side and the latter the front elevation. A is the cylinder, strengthened above and below by the belts, B and a. The bottom plate of the cylinder, which is movable, is supported by the hooks, c. This plate is removed when required by means of springs fitting on D, and acting on two of the hooks, c, so as to withdraw them from under the grating, b. Upon a lies a second ring, d, supporting the handle, e. The tops of the

hooks, c, lie upon four inclined planes fixed on the ring, D. The action is as follows:—On turning D to either hand the plate, b, which is covered with a suitable straining cloth or tissue of very fine wire gauze, is brought close up to the end of the cylinder, and if this is then filled with the colour to be strained, and the piston, M, worked by the pulley, E, the wheels, F, G, H, I, K, and the rackwork, L, presses it through the filter. It is possible that an adaptation of the Needam filter press might answer the same purpose.

The subject of thickeners has been already discussed on pp. 17, 66, and 75, to which the reader is, therefore, referred. A few additional remarks are, however, needed. Certain thickenings, such as flour and starch, are insoluble in cold water, others, like the gums, are soluble in cold water, while certain mixed thickeners are partially soluble only. These distinctions are highly important as to their action. A smaller weight of the insoluble thickenings will produce as high a degree of tenacity as a larger of the soluble class. The following quantities may be regarded as respectively equivalent:—

 Starch
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 <t

As a rule the smaller the quantity of thickening needed the darker is the resulting colour. What may be called the penetrating power of different thickeners is also a point of importance. Generally speaking, the more the colours can be kept to the face side of the cloth, and prevented from penetrating into the thickness of the tissue, the greater is the economy, and the finer and clearer the effects produced. Great judgment is required in combining various thickeners together for any desired effect. Combinations unskilfully made often separate, and in consequence work badly. Chemical combination between the thickening on the one hand, and the colours or mordants on the other, is to be avoided as far as possible. It produces loss, and may sometimes totally spoil a colour. Saccharine matters cannot be safely added as thickeners to colours containing metallic salts, since they hinder the combination which would otherwise take place between the mordant and the metallic colouring matter. Starch, likewise, if used to thicken very acid colours, may, on standing for a few days, become partially converted into starch-sugar or glucose, and may then have the effect of masking the mutual reactions of the various ingredients. As an interesting instance of such "masking," we may mention that a sample of nitrate of iron has been known to produce no black colouration when mixed with logwood or gall-liquor. A strong smell of bitter almonds explained the mystery. The nitric acid used in preparing the nitrate of iron was mixed with a residual product from the manufacture of nitro-benzol, and a small quantity of the latter body effectually prevented the reaction of the nitrate of iron and the tannin.

From such instances it will be seen that no collection of receipts, however varied, complete, and valuable, will suffice to make a colour-mixer. Extensive chemical knowledge, long experience, a habit of minute and accurate observation, and great fertility in resources are needed.

The styles of calico printing are roughly grouped under eleven heads. "Roughly," we say, since each of these has its subdivisions and its modifications, and since many effects are produced by a combination of processes

belonging to two or more styles, to each of which they might with equal justice be ascribed. These styles are—

I. Madder Colours, with several Variations.

In its plainest form one or two mordants—namely, red liquor and iron liquor—are printed on the goods, which are then dyed in the madder-beck. The result is a white ground, with a pattern which may be black; red; black and red; black and two shades of red, the red liquor having been applied in different strengths; red, black, and purple, the purple being produced by iron liquor weaker than is required to give a black. Chocolate may be added by causing both red and iron liquor to be applied to the certain parts of the design. Brown is also obtained by the introduction of catechu.

Another variation of the madder style is more complicated:—Iron liquor, red liquor, or combinations of both, are printed on, and also lime-juice, technically called "acid." The piece is then printed over—technically called "covered"—with a fine pattern, in purple or light chocolate, and dyed up with madder. The red mordant used in this process is of a peculiar kind, known as resist-red. Where the resist-red and the lime-juice have been printed on, the purple and chocolate are prevented from fastening, and there remain, consequently, pure red and clear white portions, whilst the rest is taken up with the fine cover pattern. Sometimes a very weak purple is "blotched" or padded all over, when the only white portions remaining are those where the acid has been printed on. This style obviously admits of the production of a great diversity of effects.

A further variation is the French pink style, which consists entirely of different shades of red and pink. Red mordant of different strengths, if more than one shade of red or pink be required, are printed on, and also acid (limejuice) for the production of whites. The whole may then be either "covered" or blotched with the appropriate mordant for a very pale red. The whole is then dyed in the madder-beck and cleared with soap, as will be described below. All the variations of the madder style produce fast colours, which, in domestic phraseology, wash well.

II. Garancin Colours.

This style is very similar to the preceding, garancin being used instead of madder. The colours used are generally heavier and darker, deep reds, browns, and oranges predominating. Catechu is largely used as an accessory. In this style the goods do not undergo a final treatment with soap, and the colours are less permanent than those dyed with madder.

III. Reserved Style.

This style may be termed a combination of either of the two former with the eighth (Steam-Colour Style). After the madder-work has been dyed and cleared, a further design—in yellow, blue, or green—is blocked in, and fixed by the steaming process. Sometimes a "resist paste" is blocked on, so as to protect the whole or certain portions of the pattern originally produced, and a small pattern in drab, slate, buff, &c., is printed over-all. Or, instead of colours mordants are printed on in like manner, and the goods are subsequently dyed in cochineal, bark liquor, &c., which of course only take effect where

these mordants have been attached. Sometimes white portions are protected by the reserve paste, and various lively colours are subsequently blocked in upon these. This style produces an extreme variety of effects.

IV. Padding Styles.

The whole cloth is padded all over with a suitable mordant. A design is next printed on in acid (discharge), and the goods are dyed. The result is white spots—when the acid has been printed on—upon a ground of one uniform colour. Upon the white discharged spots steam-colours or pigment-colours may again be printed.

V. Indigo-Blues.

A reserve paste, which may be accompanied by so-called yellow or orange mordants (see below), is printed upon the goods, which are then dyed up to the required shade in the indigo-vat. The indigo is not deposited upon the spots where the reserve has been printed. Yellows and oranges, where required, are brought out by passing through a solution of bichrome, which combines with the salt of lead contained in the yellow and orange mordants. The result is a deep blue ground colour, with designs in white, yellow, or orange, upon which, again, steam-colours may be blocked in.

VI. China Blues.

In this style mixtures containing indigo are printed upon the white cloth, and the indigo is then fixed, producing a blue design upon a white ground.

VII. Turkey Red with Discharges.

The cloth is first dyed Turkey red, upon which certain discharge mixtures are printed. The goods are next worked in a solution of bleaching-lime, which, acting where the mixtures have been printed on, disharges the red. The result is, consequently, a white design upon a red ground. But along with the discharge there is frequently printed, on a pigment-colour, a mixture for a black, or a salt of lead. In the latter case the pieces are subsequently passed through a solution of bichrome, which brings up a yellow. This style may therefore show designs in a variety of colours, the ground being always Turkey red.

VIII. Steam-Colours.

The goods in this style are generally prepared with a per-salt of tin, by means of working in a solution of stannate of soda, followed up by a passage through a dilute acid liquid technically called "sours." The mixtures printed on consist of colouring matters,—often extracts of dye-woods,—mordants, acids, and salts. After printing, the pieces are exposed to steam in an apparatus described below, washed, and dried. This style is peculiarly applicable to animal fibre,—woollen and mixed tissues, and frequently also silks, are thus treated. It is also the general style for the coal-tar colours.

IX. Spirit-Colours.

These agree in their general character with steam-colours, but contain larger proportions of acids and metallic salts. After printing they are not steamed, but merely dried very carefully, exposed to the air for twenty-four to forty-eight hours, and washed.

X. Bronzes.

This style, formerly much admired, but now falling into disuse, has for its main feature a ground colour of peroxide of manganese, upon which suitable discharges, pigments, &c., were printed on. The manganese-brown was thus removed or replaced, the result being a white, yellow, green, pink, &c., pattern on a deep brown ground.

XI. Pigment-Colours.

In this style colours ready-formed and insoluble, such as those used by artists, are fastened upon the fibre by the aid of mediums,—which might rather be called cements than mordants,—such as albumen, the fixation being completed by steaming.

First Style.-Madder.

The madder styles have for a long time played the most important part in calico-printing. A leading characteristic of these styles is that the mixtures printed on to the calico—the "colours," technically so-called—are not colours, but mordants, capable of combining both with the tissue and the colouring matter, and modifying as well as fixing the latter. The most important mordants in the madder style are the acetates or pyrolignites of alumina and iron.

No. 1. Red Liquor.—See p. 277.

No. 2. Black Liquor, or Iron Liquor.—See p. 291.

No. 3. Purple Fixing Liquor .-

Boil till the arsenic is dissolved, and let the solution stand till any turbidity is deposited. Decant off the clear.

No. 4.	Purp	le Assisi	tant	Liqu	or	(Mer	cer	and	Barr	nes's	Pa	itent).—
	Potato	starch										100 lbs.
	Water											37½ gals
			- 0	CTO								

When the reaction is over and the nitric acid destroyed add—

Pyroligneous acid 50 lbs.

No. 5. Purple Fixing Liquor .-

Dissolve at a boiling heat, and add-

Crude acetic acid (pyroligneous), at 120° F... .. 50 gals.

Allow the whole to stand for a few days; draw off the clear liquid, and add—

Spirits of salt, at 32° Tw. 3 quarts.

	THE STATE OF THE S	50/
No. 6	i. Black (Machine).—	
	Iron liquor, at 24° Tw 4 gals.	
	Pyroligneous acid 4 ,,	
	Water 4 ,,	
	Flour 24 lbs.	
Work u	p the flour with a little of the liquids into a smooth, thin paste, p	er-
	ee from lumps or clots; add the rest of the liquid, boil, and add—	
,	Oil r pint.	
No. 7	. Black (Machine) Garancin.—	
,	Water	
	Iron liquor, at 24° Tw 3 ,,	
	Purple fixing liquor, No. 5	
	Flour	
	Oil	
See also	o p. 291.	
No. 8	B. Brown Standard.—	
	Water 50 gals.	
	Catechu 200 lbs.	
Boil for	six hours, and add—	
	Acetic acid 4½ gals.	
	Water, to make up 50 gals.	
	whole stand for two days, and decant the clear. Heat it to 130°	F.,
and add		
Dissolu	Sal-ammoniac	
	e, and let settle for forty-eight hours. Decant the clear, and thick bs. gum Senegal per gallon.	ken
No. g	o. Brown (Machine).—	
	No. 8	
	Acetic acid 2 quarts	
	Gum Senegal water (4 lbs. per gallon) gal.	
No. 7	co. Acetate of Copper (referred to in No. 9).—	
140. 1	Sulphate of copper 4 lbs.	
	Acetate of lead 4 ,,	
	Hot water I gal.	
Dissolv	e, allow the turbidity to subside, and dilute to 16° Tw. with water.	
No. I	1. Brown (Machine).—	
	No. 8 7 gals.	
	No. 10	
	Gum red (see below, No. 12) 1½,,	
No. 1	2. Gum Red.—	
	Red liquor, at 18° Tw	
	Gum-substitute	
Boil up,	and stir well till all is dissolved.	
No. I	3. Brown (Machine) Garancin.—	
	No. 9 2 gals.	
	Gum-substitute water (at 4 lbs. per gallon) 1 gal.	

No. 8 2 gals. Gum substitute water (at 4 lbs. per gallon) 3½,,

No. 14.-

	Acetic acid								3 quarts
	No. 10								3 ,,
No. I	. Madder Brown	Standar	d (ar	othe	r, se	e No	. 8).		
	Water							7	o gals.
	Catechu							35	o lbs.
Boil for	ten hours; then a	.dd -							
	Sal-ammoniac							10	,,
	Acetic acid							• •	9 gals.
	Gum Senegal (gr	ound) as	requi	red t	o th	icker	١.		
No. 1	6. Brown Colour	from abo	ove.—	-					
	No. 15								2 gals.
	Acetic acid								I pint
	Acetate of coppe	r (No. 10)	• •			• •	• •	2 pints.
No. 1	7. Medium Brow	n							
	Catechu								2½ lbs.
	Sal-ammoniac								6 ozs.
				* *	• •	* *	• •		r quart.
Boil till	dissolved, and ad		200						
	Nitrate of coppe								I2 OZS.
	Acetate of coppe		,				• •		8 ,,
	Gum water					• •			½ gal.
No. 1	8. Madder Brow			-		-		-	
	Catechu								
	Sal-ammoniac Lime-juice, at 8°								4 ,,
	Nitrate of coppe								ı quart
	Acetate of coppe								I ½ ,,
	Gum Senegal								r lb.
Ma	19. Brown for G								
140.	Catechu								g lbs.
	Sal-ammoniac								I 1 ,,
	Water								ı gal.
Boil, st	rain, and add-								
2011, 11	Gum water (at 4	lbs. per	gallo	n)					1½ gals.
	Nitrate of coppe	er, at 84°	Tw.						r quart
	Acetate of copp	er (No. 1	0)						ı ,,
Lighte	r browns can be ob	tained by	y incr	easii	ng th	ne pr	opor	tion (of gum-water. A
	tone, when requir				ling	ı qu	art	of rec	l liquor to about
10 qua	rts or more of the	above co	olour.						
No.	20. Medium Bro	wn (for C	aran	icin).	_				
	Catechu								3 lbs.
	Sal-ammoniac								IO OZS.

Water 2 quarts

Gum-water	Boil, str	ain, and add—								
Acetate of copper (No. 10).		Gum-water							r gal.	
No. 21. Brown (Garancin).— Catechu 2 lbs. Water									11 pints	5
Catechu		Acetate of copper (No.	10)						11 gills	
Water	No. 21	. Brown (Garancin)								
Sal-ammoniac Sal-ammoniac Sal-ammoniac Gam-water Gum-water Gum-water Gum-water Gum-water Gum-water Gum-water Gum-water Gum-water Gam-water Gam-wat		Catechu							2 lbs.	
Boil, strain, and add— Gum-water									53 ozs.	
Gum-water 106 ozs. Nitrate of copper, at 80° Tw. 16½ Acetate of copper ½ pint. Red liquor may be added to give a redder tone. No. 22. Brown for Madder.— Catechu 2 lbs. Weak acetic acid 1 quart Sal-ammoniae ½ lb. Acetate of copper 1 pint. Decant the clear liquor for use. (See also p. 292). No. 23. Chocolate (Machine).— Iron liquor, at 24° Tw. 3 gals. Red liquor, at 18° Tw. 9 Flour 24 lbs. Oil 1 pint. No. 24. Chocolate.— Iron liquor, at 24° Tw. 1 gal. Red liquor, at 18° Tw. 6 gals. Flour 14 lbs. Oil 1 gill. No. 25. Chocolate for Garancin.— Red liquor, at 18° Tw. 4 gals. Iron liquor, at 8° Tw. 4 gals. Iron liquor, at 8° Tw. 1 lbs. Logwood liquor, to sighten 1 pint. The reddest chocolate in regular use is made with about 1 quart of iron liquor, at 24° Tw., to 30 quarts of red liquor, at 18° Tw. No. 26. Drab (Machine).— No. 8				• •					бۇ "	
Nitrate of copper	Boil, str	·								
Acetate of copper										
Red liquor may be added to give a redder tone.										
No. 22. Brown for Madder.— Catechu 2 lbs. Weak acetic acid I quart Sal-ammoniac							• •	* *	} pint.	•
Catechu 2 lbs. Weak acetic acid 1 quart Sal-ammoniac 1 lb. Acetate of copper 1 pint. Decant the clear liquor for use. (See also p. 292). No. 23. Chocolate (Machine).— 1 pint. Iron liquor, at 24° Tw. 3 gals. Red liquor, at 18° Tw. 9 Flour 24 lbs. Oil 1 pint. No. 24. Chocolate.— 1 gal. Iron liquor, at 24° Tw. 6 gals. Flour 14 lbs. Oil 1 gill. No. 25. Chocolate for Garancin.— 2 de liquor, at 18° Tw. Red liquor, at 18° Tw. 4 gals. Iron liquor, at 8° Tw. 2½ Flour 10 lbs. Logwood liquor, to sighten 1 pint. The reddest chocolate in regular use is made with about 1 quart of iron liquor, at 24° Tw., to 30 quarts of red liquor, at 18° Tw. No. 26. Drab (Machine).— No. 8 No. 10 (acetate of copper) 3 gals. Protochloride of iron (protomuriate), at 9° Tw. 1 gal. If intended for garancin, 4 gals. of gum-substitute water are used. No. 27. Drab (Machine).— 10 gals.<	-			ier to	ne.					
Weak acetic acid 1 quart Sal-ammoniac 1 lb Acetate of copper 1 pint.										
Sal-ammoniae										
Acetate of copper									-	
Decant the clear liquor for use. (See also p. 292). No. 23. Chocolate (Machine).— Iron liquor, at 24° Tw										
No. 23. Chocolate (Machine).— Iron liquor, at 24° Tw								• •	I pint.	
Iron liquor, at 24° Tw.		_		aiso j	p. 29	2).				
Red liquor, at 18° Tw.	No. 23	,								
Flour									0 0	
Oil									_	
No. 24. Chocolate.— Iron liquor, at 24° Tw										
Iron liquor, at 24° Tw			• •	• •	• •			• •	i pint.	
Red liquor, at 18° Tw.									1	
Flour									0	
Oil										
No. 25. Chocolate for Garancin.— Red liquor, at 18° Tw										,
Red liquor, at 18° Tw				• •			• •	• •	5,,,,	1
Iron liquor, at 8° Tw	2	<i>y</i> .							4 0010	1
Flour										
Logwood liquor, to sighten										
The reddest chocolate in regular use is made with about r quart of iron liquor, at 24° Tw., to 30 quarts of red liquor, at 18° Tw. No. 26. Drab (Machine).— No. 8										
liquor, at 24° Tw., to 30 quarts of red liquor, at 18° Tw. No. 26. Drab (Machine).— No. 8										of iron
No. 26. Drab (Machine).— No. 8								0046	- quare	01 11011
No. 8	-			1	,					
Protochloride of iron (protomuriate), at 9° Tw	210. 20	,							a gals.	
No. 10 (acetate of copper) 3 gals. Gum-substitute water (4 lbs. per gallon) 1 gal. If intended for garancin, 4 gals. of gum-substitute water are used. No. 27. Drab (Machine).— No. 26										
Gum-substitute water (4 lbs. per gallon) 1 gal. If intended for garancin, 4 gals. of gum-substitute water are used. No. 27. Drab (Machine).— No. 26										
If intended for garancin, 4 gals. of gum-substitute water are used. No. 27. Drab (Machine).— No. 26										
No. 27. Drab (Machine).— No. 26	If intend	, ,		-		*			0	
No. 26										
Muriate of iron, at 9° Tw ½ gal. Gum-substitute water, at 4 lbs. per gallon 10 gals.		,							to gals.	
Gum-substitute water, at 4 lbs. per gallon 10 gals.		Muriate of iron, at 9° T	W						l gal.	

DIEING AND CALLED PRINTING.
No. 28. Farina Gum-Water, Dark.—
Water 5 gals.
Dark calcined farina 30 lbs. Boil well.
No. 29. Fawns.—Add to No. 26 or No. 27 $\frac{1}{12}$ th of red liquor, more or less according to the shade required.
No. 30. Purple, Madder (Machine).
Iron liquor, at 24° Tw 2 gals. No. 5
No. 5
No. 31. Purple, Madder (Machine).—
Iron liquor, at 24° Tw 2 gals.
No. 5
No. 28
No. 32. Purple (Garancin).—The following thickener is added, in various proportions, to the iron liquor:—
Light British gum 40 lbs.
Water
No. 5
Boil well together, draw off, and allow the whole to stand for three or fou days. Of this, from 8 to 30 gallons, and upwards, may be added to 1 gallon of iron liquor.
No. 33. Padding Purples.—The thickener is prepared as follows:—
Water
No. 5 2 ,,
Logwood liquor, at 8° Tw
Flour
No. 28
One part of iron liquor, at 24° Tw., is mixed with any required amount of thi thickening, according to shade required. Block-colours are made by diluting the above. (See also p. 291).
No. 34. Red (Machine), Dark.—
Red liquor, at 18° Tw 6 gals.
Flour
No. 35. Red Liquor, Standard.—
Alum
Boiling water 5 gals.
Stir up until dissolved, allow the mixture to settle, and draw off the clealiquor. (See also pp. 283 and 284.)
No. 36. Red, Pale (Machine).—
No. 35
Gum-substitute water (30 lbs. gum-substitute in 3 gals.

No. 37. Red-Resist, Dark (Machine)	_					
Resist-red liquor, at 18° Tw.						12 gals.
Flour						24 lbs.
Boil well, and when almost cold add-						
Tin crystals						
Used to resist a chocolate "cover."						
Used to resist a chocolate " cover.						
No. 38. Resist-Red Liquor						
Acetate of lime liquor, at 24° Tv						90 gals.
Sulphate of alumina					2	72 lbs.
Ground chalk						34 ,,
No. 38a. Resist-Red Liquor						
Water						I gal.
Alum						5 lbs.
						2½ lbs.
Soda crystals						1 lb.
			• •			4
No. 39. Resist-Red, Dark (Machine)						
Resist-red liquor, at 18° Tw.						
Flour				• •	• •	12 lbs.
Treat as in No. 37, but add-						
Tin crystals						3 lbs.
Used to resist a purple cover.						
D'I DITIUM						
No. 40. Resist-Red, Light (Machine).						To male
Resist-red liquor, at 5° Tw						
Flour		• •		• •		9 105.
Boil, and when cool add—						11
Tin crystals	• •		• •	• •	• •	2 lbs.
No. 40. Red, Full (Garancin)						
						5 gals.
Water						
Flour						12 lbs.
N D I Duit Committee (Mark						
No. 41. Red, Resist, Garancin (Mach						61.
Resist-red liquor, at 14° Tw.						
	• •	• •		• •		12 lbs.
Boil, and when cool add-						. 11
Tin crystals			• •	• •	• •	4 lbs.
This mixture is used to resist chocolate	cove	rs.				
No. 42. Red, Resist, Garancin (Mach	hine).					
Resist-red liquor, at 14° Tw.	,					6 gals.
Flour						12 lbs.
Boil, and when nearly cold add—						_ =
Tin crystals						21 1hc
						24 105.
Used for resisting purple covers.						

5/2 DIBING AND CALICO PRINTING.
No. 43. Red, Resist, Garancin (Machine)
Red liquor, at 18° Tw 2 gals.
Starch 2½ lbs.
Peachwood liquor r gill.
Boil, and when cool add—
Tin crystals
Used for resisting light chocolate "covers." (See also pp. 287, 288, and 289.)
Mordants, Discharges, Reserves, Covers, &c.
No. 44. Alkaline Red Mordant.—
Alum (not ammoniacal) 10 lbs.
Boiling water 5 gals.
Dissolve and add—
Caustic soda-lye, at 70° Tw gal.
Add cold water to make up 12 gals., allow the precipitate to settle, and wash
by decantation till the washings are tasteless. Filter, remove the precipitate
from the filter, and dissolve it in 5 pints caustic soda-lye, at 70° Tw. Boil,
make up to 3 gals., add 9 lbs. of dark gum substitute, and boil again.
No. 45. Light Red Alkaline Mordant.—
No. 44
Dark gum-substitute water glbs.
No. 46. Alkaline Pink Mordant
Caustic potash-lye, at 54° Tw 40 gals.
Sulphate of alumina (patent- or cake-alum) 140 lbs.
The lye is heated in an iron boiler, and the sulphate of alumina added by
degrees, with frequent stirring. The yield is about 45 gals., at 34° Tw. It is
thickened with dark gum-substitute.
No. 47. Alkaline Light Pink Mordant.—
Caustic potash-lye, at 41° Tw 25 gals.
Alum (potash) go lbs.
Dissolve in the same manner as above. (See also p. 278.)
No. 48. "Acid" (Lime-juice Mixture).—
Lime-juice, at 8° to 10° Tw 1 gal.
Starch 1 lb.
Boil, and stir till dissolved.
No. 49. "Acid."—
Lime-juice, at 20° Tw
Starch
Lime-juice, at 30° Tw
Starch I lb.
These acids are sometimes thickened with gum-substitute.
No. 51. Acid Discharge.—
Lime-juice, at 22° Tw
Bisulphate of potash
The clear liquor is run off from the sediment, filtered, and thickened with I lb.
starch.
No. 52. Acid Discharge.
Lime-juice, at 28° Tw
Bisulphate of potash 2 lbs.

Tilter and thicker with
Filter, and thicken with—
Dark British gum 5 lbs. For Reserve Pastes see Style III., Nos. 1 and 2.
No. 53. Gall Liquor.—
Gall nuts, ground 28 lbs.
Acetic acid 2 gals.
Water 12 ,,
Let stand for two days, stirring occasionally, and then filter.
No. 54. Hazel Standard.—
Brown, No. 9 I gal.
Bark liquor, at 10° Tw
Logwood liquor, at 12° Tw
Cochineal liquor, at 8° Tw
No. 55 (see below)
Gum Senegal water (at 6 lbs. per gal.) I gal. I pint.
No. 55.—
Nitrate of iron, at 80° Tw I gal.
Nitrate of copper, at 100° Tw
No. 56. Buff Standard.—
Water
Copperas
Acetate of lead (brown)
Ditto ditto (white)
No. 57. Another Buff.—
Water 5 gals.
Copperas 20 lbs.
Brown sugar of lead
The clear liquid drawn off after solution and settling is reduced to the desired
shade with gum Senegal water.
No. 58. Another Buff.—
Water 5 gals.
Copperas
Acetate of lead (brown)
No. 59. Buff (Yellower Tone).—
Water 5 gals.
Copperas
Acetate of lead
Acetic acid
No. 60. Chrome Standard (Sulphate)
Water 6 gals.
Bichromate 24 lbs.
Dissolve with the aid of heat, and put in a large stoneware pan, and add—
Sulphuric acid, at 170° Tw 6½ pints.
Cold water 3 gals.
Stir in by degrees—
Sugar 6 lbs.
When the violent reaction and frothing are at an end, boil down to 3 gals.

No. 61. Chrome Standard (Muriate or	r Chloride).—
Boiling water ,	2 gals.
Bichromate	8 lbs.
When dissolved add-	
Hydrochloric acid at 32° Tw	12 gals.
And by degrees—	
Sugar	3½ lbs.
No. 62. Chrome Standard (Arseniate))
140. 02. Chrome Standard (Arsentate)).—
Water	2 gals.
Bichrome	io lbs.
Arsenious acid (white arsenic)	14 lbs.
Hydrochloric (muriatic) acid, at	t 32° Tw 1 gals.

Heat till the bichrome is entirely reduced and the liquid is a pure green without an olive cast. Sometimes a further amount of acid is required to produce this result. When the reduction is accomplished the mixture is concentrated to 95° Tw. The chrome standards require care in their preparation; if not perfectly uniform and smooth they should be re-heated, and a little more acid added, if needful. Gum tragacanth is the best thickening material.

For a variety of "covers," see Style III., Reserves.

No. 63.	Fast	Blue	Stand	lard.—
---------	------	------	-------	--------

Water	 	 	 	 	100 gals.
Indigo (wet-ground)	 	 	 	 	12 lbs.
Copperas	 	 	 	 	16 ,,
Lime, slaked	 	 	 	 	181 ,,

The whole is let stand for two days, and stirred from time to time; then allowed to settle, and the clear liquor syphoned off is mixed with 1 pint double muriate of tin, at 120° Tw., to every 10 gals. It is then thrown upon a flannel strainer, and allowed to drain till it takes the consistence of a thick paste.

No. 64. Fast Blue (Machine) .-

No. 63	 	 	 	 	 I quart.
Tin crystals	 	 	 	 	 6 ozs.
1370400					a amarte

No. 65. Fast Blue Standard .-

Indigo, ground wet	 	 	 	8 lbs.
Caustic soda, at 70° Tw.	 	 	 	I gals
Water	 	 	 	I1 11
Feathered tin, an excess.				

Boil in an iron pan until a few drops, when placed on a pane of glass, appear perfectly yellow.

No. 66. Fast Blue (Block) .-

No. 65	 	I quart.
Tin crystals	 	12 ozs.
Lime-juice, at 60° F	 	12 ,,
Gum Senegal water, at 6 lbs, per gal.	 	a quarts.

No. 67. Fast Green.—		
No. 65		Il quart
"Lead gum" (see below)		2 ,,
Tin crystals		8 ozs.
No. 68. Lead Gum.—		
Sugar of lead, white		8 lbs.
No. 69. Drab.—		
No. 60		5 quarts.
Gum tragacanth water, at 1 lb. per gal		10 ,,
Bark liquor, at 8° Tw.		I 1 ,,
No. 70. Fawn		2 ,,
No. 60		I gal.
No. 8		½ gal.
No. 71. Slate.—		
No. 60		I gal.
		Ι 11
	No. 65 "Lead gum" (see below) Tin crystals No. 68. Lead Gum.— Sugar of lead, white Nitrate of lead Hot water Gum Senegal water, at 6 lbs. per gal. No. 69. Drab.— No. 60 Gum tragacanth water, at ½ lb. per gal. Cochineal liquor, at 4° Tw. Bark liquor, at 8° Tw. No. 70. Fawn.— No. 60 Gum tragacanth water, at ½ lb. per gal. No. 8 No. 71. Slate.— No. 60	No. 65 "Lead gum" (see below) Tin crystals No. 68. Lead Gum.— Sugar of lead, white Nitrate of lead Hot water Gum Senegal water, at 6 lbs. per gal. No. 69. Drab.— No. 60 Gum tragacanth water, at ½ lb. per gal. Cochineal liquor, at 4° Tw. Bark liquor, at 8° Tw. No. 70. Fawn.— No. 60 Gum tragacanth water, at ½ lb. per gal. No. 8

Before these mordants, technically called colours, are printed on to the calico it requires to be be called in the most thorough and complete manner (see p. 44). After printing the goods are transferred to the ageing room, see p. 280. The next process is the so-called dunging, effected either with actual cow-dung, with the dung-substitutes, or with a combination of both. For a detailed description of this process the reader is referred to p. 294. Next follows the dyeing (garanqage), see p. 299. Finally comes the clearing or brightening (avivage), see p. 312.

The Plate Style, another modification of madder work, requires a somewhat modified procedure. For a plate purple, containing black and purple only, one shade or more of the latter, print on No. 6r a purple, say No. 30, regulated according to shade, and an acid, No. 50, and pad or cover in the whole in a pale purple, No. 33. The goods are then aged, fly-dunged at 170° F., and dunged again for half an hour at 165° F. They are next washed and dyed with ground Levant madder, to which have been added 5 per cent of its weight of chalk and 3 quarts of bone-size. The temperature is raised in two hours to 175° F., at which it is kept for half an hour. They are then well washed and soaped, using 5 lbs. of soap for fifteen pieces, each 30 yards by Iths, and boiling for half an hour. It is then again well washed, and passed for five minutes through 300 gallons of water, at 140° F., to which have been added 2 quarts of solution of bleaching lime, at 8° Tw. They are again rinsed, and boiled for half an hour with 3 lbs. of soap per fifteen pieces. Next wash, and repeat the chloride of lime treatment for five minutes, using 200 gallons of water, 4 quarts solution of chloride of lime, at 8° Tw., and 2 lbs. carbonate of soda, at 160° F. Wash again well and dry.

Plate Pinks are composed of shades of red and pink only. The process is as follows:—Print on No. 34 dark red, with paler reds, as No. 36, and acid

No. 49. A very pale red mixture is padded all over. The goods are then aged for two or three days and dunged at 160° F., taking care not to use any dung substitute containing free alkali. Dye with the best French or Levant madder. The shades produced are dyed purposely too full, from 4 to 6 lbs. of Avignon madder being required per piece of $\frac{7}{8}$ cloth. If the water is soft, chalk may be added to the extent of about 5 per cent of the weight of madder. The dye-beck is steadily raised to 150° F. in two hours, and kept for half an hour at that heat. The pieces when dyed are firstly well washed and soaped at 140° F. for half an hour with $\frac{1}{8}$ lb. soap per piece. Next they are well washed in water and placed in another beck of cold water, slightly acidified with sulphuric acid or perchloride (oxychloride) of tin. The heat is gradually raised to 120° F. in about thirty minutes. When the goods show a bright orange colour they are lifted and winced in water. This process, the reduction of the reds and pinks to the depth of shade they are to have when finished, is called "cutting." The more this acid treatment is prolonged, and the higher



MADDER RED AND PINK.

the temperature, the paler the pinks become. The pieces are then put in a fresh beck and boiled with soap for an hour, lifted, washed again in pure water, and boiled with soap and water at the pressure of 2 atmospheres for two or three hours. The goods are next lifted, washed, and entered in a fresh beck of water at 160° F., to which a very little bleaching soda (hypochlorite) has been added. After ten minutes in this solution they are washed and dried.

The above specimen will serve as an illustration of the madder style.

To produce this pattern, red liquor at 12° Tw., thickened with flour, is printed in for the red, and a much weaker red liquor, similarly thickened, for the pink. The pieces are then dunged, washed, dyed with madder, cleared, and finished. (See p. 299).

The above is the first of a series of three patterns, for which we are indebted to the kindness of Messrs. Wood and Wright, of Manchester.



MADDER STYLE. (FIRST STAGE.)

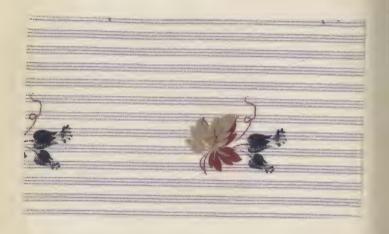
These serve to illustrate the successive stages of madder-work. In the first, the mordants, or, as they are technically called "colours,"—suitable for subsequently producing, in combination with the tinctorial principles of the dyeware, black, purple, red, and light brown designs upon a white ground,—have been printed on, and the pieces have been cleared and dunged (see p. 297, &c.), in order to remove the thickeners and saturate any mordant attached to the fibre and not yet perfectly decomposed. After this process the goods are ready to be dyed up in the madder-beck (see p. 299). The pattern below shows their condition after dyeing and a subsequent washing, but before the final clearing process. The shades are developed, but they are still deficient in brightness, and the ground, which is intended to be white, is stained a dull light red. The third, and last of the series (see next page), shows the appearance of the pieces after having undergone the clearing process. The general



MADDER STYLE. (AFTER DYEING.)

details of this operation are described in p. 309. The exact procedure followed in this case is as follows:—After washing out of the dye-beck, the pieces are next hot-watered, and then soaped at 140° F. for forty minutes. They are next washed and soaped again, in fresh baths, for the same period of time, but the temperature is increased to 160° F. They are again washed in plain water, in order to remove traces of soap, which would interfere with the next process. They are then cleared with a very dilute solution of chloride of lime, washed again in clear water, and finished. The ground is now white, and the colours of the design have lost in depth—for which an allowance was made in the original intensity of the shade—and gained in brightness.

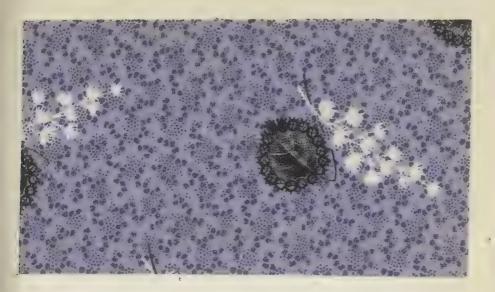
The first pattern on page 579 illustrates a different style of madder-work combined with aniline black. To produce this effect the pieces are printed first with so-called "acid,"—i.e., lime-juice,—at 8° Tw., thickened with gum-substitute (see Style I., No. 48, p. 572, and p. 318), to produce the white figure. Where this mixture is applied, the mordants, which follow next, are prevented from



MADDER STYLE. (AFTER CLEARING).

attaching themselves to the fibre; and when the pieces ultimately come out of the dye-beck, this figure is found, not dyed, but merely stained with a faint red, which is entirely removed in the clearing process, leaving a white, as shown in the pattern. The black design is next produced with aniline (see Aniline Black, p. 211), and remains unaffected during the subsequent operations. The pieces are then "covered" with iron liquor (see Nos. 30, 31, &c.) to produce the small design in dark purple, and padded all over in a weaker iron liquor (see Nos. 33) to give the light purple ground. The goods are then aged for thirty-six hours, or longer, at 80° F., dunged, washed, dyed in the nadder-beck,—which produces the two shades of purple according to the ageth of the mordants,—and cleared.

his some printing establishments on the Continent, hydrofluosilicic acid is amployed instead of citric acid.



MADDER AND ANILINE BLACK.

Second Style.—Garancin Colours.

As a general rule the effects produced with crude madder can also be obtained by the use of garancin (see p. 257). The shades, both dyed and printed, with this preparation are fully equal to madder-colours—properly so-called—in brilliance, but fall short of them in permanence and in power of resisting the action of soap, light, air. &c. They are, nevertheless, commonly classed amongst "fast colours," and are far more permanent than the shades obtained with the woods. The best qualities of garancin yield colours which will stand soaping to some extent, and which have this advantage over madder, that they scarcely stain the white unmordanted grounds, and consequently the operation of clearing (avivage) is much less severe.



GARANCIN. -

Garancin is generally employed for full, heavy patterns, and especially for combinations of black, red, and chocolate; for browns and drabs; black and scarlet; orange and brown, &c. The reason why garancin is selected in preference for heavy shades is that garancin gives up, practically speaking, the whole of its colouring matter to the water in the dye-beck, whilst crude madder yields only a part. Hence the employment of crude madder for heavy shades is costly, as a large excess must be used, which is in great part wasted, if the dregs are not subsequently converted into garanceux. The mordants ("colours," technically called) for garancin work are used weaker than those required for producing similar shades with madder. From two-thirds to three-fourths of the strength used for madder is sufficient. For further particulars relative to garancin dyeing the reader is referred to pp. 308, 496, and 497.

Garancin is very frequently associated with catechu for the production of browns and brownish-reds. This combination may be brought about in various ways. The second pattern on the previous page is given as a specimen of the class of effects produced by this style. The mordants printed on for this specimen are iron liquor, at 10° Tw., for the blacks; and for the browns, mixtures of catechu dissolved in water, with sal-ammoniac, acetic acid, and a salt of copper, the latter being added along with the thickening. The pieces are then dyed in the garancin-beck and cleared.

Third Style.—Reserved.

This style is an addition to the madder and the garancin styles. In goods printed in these styles portions of the design are often left white, and these spaces are afterwards filled in with a variety of colours, such as green, yellow, or blue, produced and fixed by the steaming process, as described below.

There is also another method of combining madder and garancin work with steam-colours. There is blocked on the dyed piece a reserve paste, such as either of the following:—

No.	I. Reserve.—						
	Lime-juice, at 50° Tw.					 	3½ gals.
	Caustic soda, at 70° Tw.					 	21 ,,
Raise	to a boil, and work up in a se	epar	ate v	esse	I		
	Pipe-clay					 	56 lbs.
	Boiling water					 	3 gals
And a	add						
	Gum Senegal water (at 6	lbs.	per g	gallo	n).		
Mix t	he two liquids, and boil for t	went	y mi	nute	s.		

NI a Deserve

110. 2. 1(030700.				
Lime-juice, at 60° Tw.	 	 	 	4 gals.
Caustic soda, at 70° Tw.	 	 	 	3 ,,
Boil and add—				
Pine-clay	 	 	 	48 lbs.

No. 1 is used to preserve reds and blacks. No. 2 is used where purples also occur.

When the reserve paste is dry small patterns are covered in with the machine with certain drabs, olives, &c. These are then dunged, and dyed with quercitron, cochineal, madder and quercitron, &c. Where the reserve has been applied, the original shade—or white spaces—will remain untouched by the subsequent or covering-colour. Where white designs have been reserved, steam-colours may now be blocked in. Among the covering shades are—

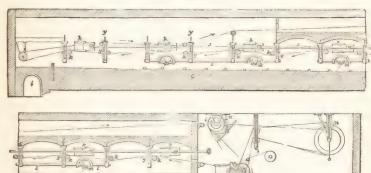
	No. 3	5 Drab.—								
		Iron liquor, at 24° Tw.			• •				0	
		Water							9 0	
		British gum, light		* *	* *				g lbs.	
	No. 4	10 Drab The same, w	ith d	oubl	e the	an	nour	t of	water and	18 lbs.
31	ım.									
	No. 5	. Drab.—								
		Iron liquor, at 24° Tw.							r gal.	
		Red liquor, at 20° Tw.							Ι,,	
		Water							5 gals.	
		British gum, light							rolbs.	
	No. 6	. Drab The same, with	IO g	als.	wate	r an	d 20	lbs.	gum.	
		Olive.—								
	,								2 gals.	
									ı gal.	
		British gum, light							6 lbs.	
	No 8	Olive.—								
	110.0	Red liquor, at 18° Tw.							a gals.	
		Iron liquor, at 8° Tw.								
		British gum, light							10 lbs.	
	D.T	3 , 3								
	No. 9.	Sage.—							1 .	
		Red liquor, at 9° Tw. Iron liquor, at 12° Tw								
		British gum, light							0	
		0 . 0		• •			• •		10 105.	
	No. 10	Sage.—								
		Red liquor, at 3° Tw							-	
		Iron liquor, at 12° Tw				• •			r pint	
		British gum, light	0 0			• •			5⅓ lbs.	
	No. II	. Chocolate.—								
		Red liquor, at 15° Tw							6 gals.	
		Iron liquor, at 24° Tw				• •			I gal.	
		British gum, light							10½ lbs.	
		Flour							3½ ,,	

Fourth Style.—Padding.

In the padding style the white calico is saturated all over, by means of the padding process, with a mordant, generally red or black liquor, or a mixture of both. It is next dyed in a specially arranged apparatus, known as a padding-flue. The design to be finally produced is then printed on in an acid, to

Before the drying-flue stands the padding apparatus. Its trough being charged with the iron liquor, or red liquor, as required, the pieces of calico are conducted twice through it, and then into the flue. Their course is indicated





in the diagram by arrows. They are next printed with the acid mixture, aged for two or three days, dunged and dyed. The following are some of the colours commonly produced in this style:—

No. 1. Claret and White.—Pad in red liquor, at 10° Tw. Dry, cool, pad again in same liquor, dry, cool, and print with the following mixture:—

After printing, the goods are aged three nights. They are next fly-dunged at a boiling heat, washed, dunged again at 160° F. for thirty minutes, washed, dried and singed, washed, and dyed. For 12 pieces, 30 yards in length, there are required—

Ground peach-wood	 	 	 	 18 lbs.
French madder	 	 	 	21 ,,
Sumac	 	 	 	 5 ,,
Logwood (aged)	 	 	 	 5 ,,

The pieces are run in the dye-beck cold for twenty minutes, and brought gradually to a boil in seventy minutes, kept at this heat for fifteen minutes, run out rinsed and washed; next branned for ten minutes, at the boiling-point, with a few pounds of bran; rinsed and branned again, washed, and dried.

No. 2. Scarlet and White.—Pad and dung as No. 1. For dyeing, take to 10 pieces—

French madder	 	 	 	 15 lbs.
Dutch crop madder	 	 	 	 15 ,,
Peach-wood	 	 	 	 7 .,
Sumac	 	 	 	 4 1,
Bone size	 	 	 	 3 quarts.

Bring to a boil in two and a quarter hours, and boil fifteen minutes. Wash and bran as in No. 1.

No. 3. Scarlet and Yellow.—The general procedure as in No. 2. The dyematerials are, for ten pieces,—

French madder	 	 	 	 22 1 lbs.
Dutch crop madder	 	 	 	 221 ,,
Sumac	 	 	 	 71 ,,

After dyeing, the pieces are washed, branned, and dried; then padded in red liquor, at 16° Tw.; aged for two nights, fly-dunged at 130° F., washed in warm water at 120° F.; then re-dyed in 20 lbs. quercitron bark per 10 pieces, raising the heat to 120° F. in one hour, keeping at that temperature for fifteen minutes; then washing and drying.

No. 4. Burgundy and White.—Pad, &c., as in No. 1. For dyeing 10 pieces take—

French madder	 	 		18 lbs.
Peach-wood	 	 		18 ,,
Logwood	 	 	 	 1 1 ,,
Sumac				
Glue				

Raise to a boil in one and three-quarter hours; keep up the boil for fifteen minutes; wash and bran for ten minutes at a boil, wash, and dry.

No. 5. Tyrian Purple and White.—Pad and prepare as in No. 1. For dyeing, to 10 pieces, take—

Logwood	 	 	 	 5 lbs.
Dutch madder (crop)	 	 	 	 5 11
Peach-wood				
Bran				
Bone size				

Raise to 212° F. in one and three-quarter hours; keep at that heat for fifteen minutes. Wash and bran for five minutes at 150° F., using 1 lb. bran per piece; wash, and dry.

ducing non-so-sinons tolo-

-	dyeing, per 12 pieces, take—
	Cochineal, finely ground 3 lbs.
	Gall-nuts r lb.
	Logwood 4 lbs.
	Peach-wood
	Raise to 170° F. in one hour and twenty minutes, and keep for ten minutes at
	that heat. Wash, and bran for ten minutes at 160° F.; then wash and dry.
	No. 7. Amber and White.—Pad as in No. 1. For dyeing 10 pieces take—
	Quercitron bark 20 lbs.
	Dutch madder (crop) ,
	Bone size 2 quarts.
	Raise temperature to 160° F. in seventy-five minutes, and maintain that heat
	for fifteen minutes. Then wash, and bran at 150° F. for ten minutes. Wash
	and dry.
	No. 8. Peach and White.—Pad, &c., as in No. 1. For 10 pieces take—
	Cochineal, ground 2 lbs.
	Peach-wood 2 ,,
	Logwood 6 ozs.
	Raise to 140° F. in one and a quarter hours; wash and bran at same tem-
	perature for ten minutes; wash and dry.
	No. 9. Black and White.—Pad once in red liquor at 20° Tw.; print design
	with the following discharge:—
	Lime-juice, at 22° Tw
	Bisulphate of potash

Strain, and thicken the clear liquor with-

After printing, age for three nights, fly-dung at 212° F.; give a second dunging, at 140° F., for twenty minutes. Wash, dry, singe; wash again, and dye with, per 10 pieces,-

> Logwood 60 lbs. Bone size 4 gals. Carbonate of soda, crystals 6 ozs.

Raise to 212° F. in seventy minutes; wash and dry.

No. 10. Olive, Drab, &c., and White .- For drabs, pad in iron liquor diluted according to the shade, and dye in bark, or bark and logwood. For the former, per 10 pieces, use-

Quercition bark 25 lbs. Bone size 3 quarts.

Raise the temperature to 190° F. in ninety minutes, and maintain that heat for ten minutes. Wash, and bran for ten minutes at 160° F; wash and dry. For the mixture of bark and logwood, per 10 pieces:

> Quercitron bark 20 lbs. Logwood 30 ozs. Bone size 3 quarts.

The heat is regulated as in bark-dyeing.

For olives, pad in mixtures of red liquor and iron liquor.

The white, &c., patterns obtained by this style may be diversified by means of steam-colours blocked in.

Fifth Style.-Indigo Effects.

The combinations of colour produced by this style are—(1). Blue and white. (2). Blue and yellow, or orange. (3). Blue, two shades. (4). Blue, two shades, and white. (5). Blue, two shades, white, yellow, or orange. (6). Dark blue and green. (7). Blue, two shades, and yellow.

The first of these varieties is produced by printing upon the cloth certain "reserves," and then dyeing in the vat to the shade required. The design

then appears in white upon a blue ground.

Soft soap ...

No. 1. Reserve for Block-work		
Sulphate of copper	3 lbs.	
Water	I gal.	
Pipe-clay	15 lbs.	
Beat up with some of the solution, and mix gradually to then add-	a smooth paste	,
Gum Senegal water, thick	ı gal.	
Nitrate of copper, at 80° Tw	I quart.	
No. 2. Reserve (Machine).		
Sulphate of copper	21 lbs.	
Water	I gal.	
Flour	9 lbs.	
Dark British gum	2 ,,	
No. 3. Reserve (Machine)		
Sulphate of copper	5 lbs.	
Sugar of lead, white	2 ,,	
Water	2 gals.	
Dissolve, draw off the clear, and thicken with-		
Flour	3 lbs.	
Pale British gum	2 ,,	
Cool, and add to every 2 gallons-		
Nitrate of copper, at 80° Tw	½ pint.	
No. 4. Reserve (Machine)		
Sulphate of copper	8 lbs.	
Boiling water	2 gals.	
Sugar of lead, white	4 lbs.	
Dissolve, let settle, and decant the clear, and to 12 gals. of	this add—	
Flour	4 lbs.	
Pale British gum	2 ,,	
Boil, and add—		
Sulphate of zinc	2 lbs.	
The following mixtures serve to resist lighter vat-blues:-		
No. 5. Reserve, Mild, for Block		
British gum, dark	25 lbs.	
	15 quarts.	
Boil for ten minutes, and add-		
•		

500	DYEING	AND	CALI	CUr	KIIV	1 1 1 1 1 1	J,
When the	proughly incorpora	ted add-	_				
5	Sulphate of zinc						20 lbs.
	in, and add—						
	Pipe-clay						rolbs.
	Water						
1	Nitrate of copper,	at 80° T	w				7½ gals.
Mix all th	noroughly together	•					
No. 6.	Reserve, Mild (M	achine).					
1	British gum, dark						. 8 lbs.
	Water						· 34 quarts
Boil, and	add—						
	Soft soap	: • • •					. 2 lbs.
When co	ol add—						
	Sulphate of zinc						. 6 lbs.
	Boiling water						. ½ gal.
	Nitrate of copper,	at 80° 7	Cw.				. I quart.

After the reserve paste is printed on, the goods are hung in a somewhat damp atmosphere for forty-eight hours, and then dyed blue in the vat.

For yellow or orange designs upon a blue ground the following pastes are used as reserves:—

No. 7. Yellow									
Sulphate of copper									20 lbs.
Water									2 gals.
Nitrate of lead									20 lbs.
Dissolve, and thicken with—									

Boil all well together.

N.B. The sulphate of lead here mentioned is the sediment left on making red liquor with sugar of lead and alum (or sulphate of alumina), after running off the clear liquid.

No. 8	, Orange	2.—A	sta	ndar	d is	mad	e as	tollo	ws:	_	
	Sugar of	lead	, w	hite							 24 lbs.
	Water										 6 gals.
	Add lith	arge									 12 lbs.

Stir the litharge in gradually till it is perfectly white; allow the sediment to subside, and use the clear liquid. This is used instead of the water directed in No. 7. After dyeing in the vat, the pieces are passed through sulphuric acid sours, then well washed, and passed for ten minutes through a solution of bichromate, at 100° F., containing 2 ozs. of this salt per gallon. The pieces are next well washed in water, and then winced in water and muriatic acid, at ½ Tw., to which 1 oz. of oxalic acid per gallon has been added. This treatment brightens the yellow design, and removes any trace of green that may remain. The goods are then washed and dried.

In case of orange, the pieces after treatment in the oxalic-muriatic bath, are washed and winced in the following mixture, at the temperature of ISO° F.:—

When the orange pattern appears full and bright, the pieces are lifted, washed thoroughly, and dried.

For two shades of blue: a pale blue—the lighter of the two shades—is first given to the whole pieces in the vat. They are then taken out, well rinsed in water, then passed through a sour (sulphuric acid at 2° Tw.); washed again, squeezed, and dried. One of the reserves—Nos. 1, 2, 3, or 4—is then printed on, and the pieces are dipped again to the darker shade, and finished as for white on a blue ground. The result is a pale blue design on a dark blue ground.

For two shades of blue along with white, a design is printed in chloride of manganese (muriate of manganese), thickened with British gum (dark), and raised with soda and chloride of lime, as in the "Bronze" Style. The pieces are then dried, and a further pattern blocked in with the reserve No. 1. They are next limed, and dyed in the vat to the required shade, lifted, hung up to oxidise, washed again, and winced in a sour of weak muriatic acid with the addition of a little muriate of tin, washed again, and dried. The result is a pale blue ground, showing a pattern in dark blue, where the indigo is superimposed upon a bottom of manganese-brown, and in white where the reserve has been applied.

For two shades of blue, white, and yellow or orange, the process is begun as in the case just described, only, in addition to reserve 1, No. 7 or 8 is also blocked in. After passing the pieces through a sour of sulphuric acid, the yellow or orange is raised with bichromate, as directed under "blue and yellow."

For blue and green No. 7 is printed on, and the pieces are dyed a full blue. They are then soured in dilute sulphuric acid, chromed, but not of crewards passed through the oxalo-muriatic beck. The yellow combining with the blue will form a green.

For two shades of blue and one of green, the pieces are first dyed a light blue. No. 5 or No. 6 is then printed on, and No. 8 to yield an orange. The goods are then dyed, washed, soured, and chromed, and passed through very dilute nitric acid. Where the white resists have been printed the sky-blue remains, whilst No. 8 on the blue ground produces a green. The rest is dark blue. If the nitric acid is too strong the indigo may be discharged.

Another indigo effect is the Lazulite or "neutral" style, at present little in request. Mordants with reserves are printed in; the pieces are then dipped blue, when the printed portions repel the blue, and are dyed with madder. Of this style there are two modifications: where mordants for red, chocolate, or black, are printed along with a resist-white, and the pieces dyed a light blue, the resist-white being in this case required to resist the blue only; and secondly, where the white has to cut through the madder shades as well as the indigo. Some of the colours for the former variety are here given:—

No. 9. Black (for Machine Work)	
Logwood liquor, at 12° Tw	I gal.
Gall liquor, at 9° Tw	
Red liquor, at 20° Tw	-
Iron liquor, at 24° Tw	I ,,
Acetic acid	. I ,,
Flour	3 lbs.
Starch	½ 1b.
Boil well together, and add-	
Gallipoli	I pint.
Turpentine	•
No. 10. Chocolate (for Machine)	
Red liquor, at 12° Tw	2½ gals.
Iron liquor, at 24° Tw	
Sulphate of coppper	- 0
Nitrate of copper, at 100° Tw	
Flour	*
British gum (dark)	
No. II. Chocolate (Block)	
Red liquor, at 12° Tw	2½ gals.
Iron liquor, at 24° Tw	
Sulphate of copper	
Nitrate of copper, at 100° Tw	
Pipe-clay	~ ^ ^
Work up the pipe-clay well, and add—	
Gum Senegal water, at 5 lbs. per gal	Il gals.
No. 12. Dark Resist-Red (for Block Work)	- 0
Red liquor, at 22° Tw	1 gal.
Sugar of lead, white	
Sulphate of copper	41 11
Dissolve, and mix up in it-	1.0
Pipe-clay	63 lbs.
Meantime the following mixture is made separately:	
Red liquor, at 12° Tw	2 quarts.
Flour	
Heat, and when boiling add-	
Soft soap, melted	
When thoroughly dissolved add the former mixture, and	next-
Red liquor, at 2° Tw	½ gal.
Thickened as required with gum Senegal.	
No. 13. Dark Resist-Red (for Machine Work)	
Nitrate of zinc, at 36° Tw	5 gals.
Water, sightened with peachwood	2½,,
Alum	-
Acetate of lead	
Heat till dissolved, and keep stirring while cooling, when	thicken with-
Flour	
British gum (dark)	I½ ,,

For lighter shades the alum and sugar of lead are proportionately reduced (See also p. 474.)

No. 14. Brown Resist .-Catechu 24 lbs. Sal-ammoniac Water Acetic acid I gal. Boil for a quarter of an hour, and add-Gum water 71 gals. Nitrate of copper, at 100° Tw.

No. 15. White Resist.— See Nos. 5 or 6.

The pieces after ageing for seventy-two hours, and dipping to the required shade in a vat composed of—Indigo, 120 lbs.; copperas, 135 lbs.; and lime, 150 lbs. to 1000 gals. water, are washed, dunged for a quarter of an hour, at 160° F., washed again, and dyed up with madder or garancin.

In the other modification of the lazulite style the following whites are used:-

No. 16. Lazulite White (Block) .-

 Lime-juice, at 30° Tw.
 3½ gals.

 Water
 ½ gal.

 Sulphate of copper
 9 lbs.

 Pipe-clay
 48 lbs.

 Lime-juice, at 30° Tw.
 1½ gals.

Separately thickened with gum Senegal before adding it to the rest. (See also p. 474.)

No. 17. Ditto for Machine .-

In this style the lazulite or neutral whites are first printed in, and when perfectly dry the other reserve colours are printed over them. If a white under the blue alone is wanted, Nos. 5 and 6 (of this style) may also be printed. The pieces are then aged, dyed blue, washed, dunged, dyed with madder or garancin, soaped, and washed. The effect may then be further diversified by blocking in steam, spirit, or pigment colours.

It must be remarked that indigo, in whatever manner applied, though it yields fast colours, is always dull, and never produces a pleasing effect upon calico. Its use is, therefore, ordinarily confined to the lower qualities of printed goods.

The three following patterns are a combination of indigo with other colours. In the first stage we see a dark vat blue, on which a lighter blue design has been "reserved."

In the second stage a discharge has been printed on, so that the pattern now shows a design both in light blue, and in white upon the original dark blue ground. Finally, other colours are produced upon the white portions. The red is madder; the yellow portions are chromate of lead, which also produces the green when applied upon the blue portions, and the orange when applied upon the reds. These patterns have been printed at the establishment of Messrs. Wood and Wright.

The following method of applying indigo, simultaneously with mordants for madder and garancin, producing thus a variety of novel and striking effects, was invented and patented by Mr. J. Lightfoot (Specification No. 3668, Dec. 26, 1867). The patentee prepares a pulp of indigotin and tin by any of the following methods:—He takes dry indigo, ground and prepared, 1½ lbs., or if indigo-pulp is used such a quantity as may be equal to that weight of dry indigo; tin crystals, protochloride of tin, 1½ lbs.; caustic soda, at 30° Tw. (or caustic potash, at 40° Tw.), 1 gal. These materials are put in the colour pan, and raised to a boil in half an hour, when 1 gal. of boiling water is added. The mixture is then allowed to become quite cold, and 3 gals. of cold



INDIGO STYLE. (FIRST STAGE).

water are added, in which ½ lb. sugar has been previously dissolved. To this solution he adds 2½ pints of muriatic acid, at 32° Tw., or 1 pint of ordinary sulphuric acid, previously diluted with 1 pint of water, and allowed to stand till clear and cold; or 3 quarts of acetic acid at 8° Tw. The indigotin may also be precipitated by a mixture of protochloride of tin solution (double muriate), at 120° Tw., with any of the acids above named, taking ½ pint of of the tin solution to half the quantities of acids given above. Of all these precipitants, acetic acid alone is preferable. The indigotin precipitate is filtered through a deep conical filter, leaving as small a surface exposed to the air as possible. The pulp from the above quantities, when filtered, should measure about 1 gal.

To make a blue colour for printing the patentee takes 4 gals. of the above indigo-precipitate and 14 lbs. gum Senegal in powder, stirring till dissolved: the colour when strained is ready for printing.



INDIGO STYLE. (SECOND STAGE).

For a green colour he takes 4½ gals. of indigotin precipitate; 18 lbs. powdered gum Senegal, stirring till dissolved; 11 lbs. of nitrate of lead and 11 lbs. white sugar of lead, both in powder, are then added; the mixture is stirred till all is dissolved and strained.

Compound colours are made by mixing the blue and green colours with each other, or with the ordinary mordants for dyeing. With the blue and green above described, and with the ordinary iron and alum mordants (as used for madder and garancin work), the inventor prints calico, and after cooling, ages the pieces for one night. They are then fixed by passing them into a solution of silicate of soda at 8° Tw., or silicate of potash, at 12° Tw., to which 1 oz. powdered chalk is added per gal.; or into a mixture of silicate of soda or silicate of potash, at 8° Tw., with carbonate of potash at 12° Tw. This bath is heated to 90° F. in a cistern fitted with rollers at top and bottom. The pieces pass



INDIGO STYLE, WITH OTHER COLOURS. (THIRD STAGE).



STYLE PRODUCED BY LIGHTFOOT'S PATENT PROCESS.

through this solution at the rate of 25 yards per minute. After this the pieces are winced in a pit of cold water fitted with a reel about 4 feet above the surface. By this process the indigotin attached to the fibre is rendered blue. If the green mixture has been printed on the pieces are next passed into a solution of bichrome containing 1 oz. of bichromate of potash per gal. of water, at 100° F. for five minutes, when the goods are washed. The pieces are next submitted to "second dunging" for fifteen to twelve minutes, in a beck containing cow-dung and water, at 100° F. They are then washed in water, and dyed with madder, munjeet, flower of madder, garancin, extract of madder, cochineal, mixtures of garancin with sumac and bark. The grounds are then cleared in the ordinary manner, preferably with chloride of lime as applied to garancin colours.

The above and following patterns, which we owe to the courtesy of Messrs. Grafton and Co., are produced by Lightfoot's patent process.



STYLE PRODUCED BY LIGHTFOOT'S PATENT PROCESS.

Sixth Style.-China (Indigo) Blues.

This style produces blue figures on a white ground, and is therefore the reverse of Style V. A mixture containing indigo is printed on, and is then fixed by further treatment. The standard colour is made as follows:—

No. 1 .-

Indigo	 		45 lbs.
Iron liquor, at 24° Tw.	 `	 	9 gals.
Copperas	 	 	18 lbs.

The mixture is ground in an indigo mill for three days, or till perfectly smooth and uniform, and is then further mixed with—

Gum Senegal water, at 6 lbs. per gal. 7½ gals.

The whole is then ground together for an hour, and the mill is finally washed out with I gal. or It gals. of hot water, and the washings added. To reduce this standard to the shade desired, the following mixture, technically called "China blue gum," is used.

No. 2.-

Gum Senega	l wa	ter,	at 3	lbs.	per	gal.		 	2 gals.
Copperas	+2			<i>i</i> .			i e	 	₫ lb.

Other standards are occasionally employed for the same purpose, such as :-

No. 3. Dark China Blue .-

Indigo			 	 	 	 12 lbs.
Iron liquor, a	t 22°	Tw		 	 	 23 gals.
Copperas			 	 	 	 12 lbs.
Orpiment			 	 	 	 3 ,,

The first two ingredients are ground together for about three days, the others added, and the grinding continued for three days more. Gum water is then added to the extent of 3 gals., and the grinding is resumed until the colour is quite uniform. This standard is reduced to the shade required with gum water.

No. 4. Resist for China Blues .-

Sulphate of copy					
Acetate of lead	 	4.0	 	 	 4 11
Water					
Flour	 		 	 	 5 lbs.

Boil, and when almost cold add-

Nitrate of copper	in crystals	 0.4	0.0	 	To lbs.
Lime-juice, at 36°	Tw	 		 2.0	2 quarts.
(See also p. 484).					

After the pieces have been printed and aged, the pieces are dipped alternately in lime-water and in a copperas vat, standing at $r\frac{1}{2}$ ° Tw. The time of each dipping varies from fifteen to forty-five minutes, according to the shade required, and the number of dippings in each vat may be as low as four and as high as eight. They are next well rinsed in water, passed into sulphuric acid sours, the strength of which may run as high as g^c or 10° Tw., and left there till the

whites are cleared. The pieces are then well washed, and next cleared in a soap-beck, at 120° F., for fifteen minutes, using about 4 ozs. soap per piece. After again washing they are passed into weak sulphuric sours, 1° Tw., at 100° to 110° F., washed again, and dried.

The prolonged dippings involve a great outlay of time and labour and render the China blue style costly. A saving of expense is effected by forming the dippings by machinery instead of by hand, but the quality of the work is inferior. In addition this style does not admit of the highest degree

of sharpness and delicacy of design.

A process which admits of the execution of delicate patterns is the white discharge style for indigo blues, invented by Mr. J. Mercer. The process is begun by dyeing the pieces in a uniform blue in the vat, generally a medium shade. They are next washed and padded with a solution of bichrome, at 6° T. They must now be dried in a current of cold air, and in the shade, sunshine—or even strong indirect light—and an elevated temperature being equally fatal to success. They are then printed with the following:—

No. 5. White Discharge .-

Water			. ,	٠	 	 	 	 	I	gal.
Flour					 	 	 	 	2	lbs.
Dark B	ritis	h o	חווכ	n					2	

Boil up and mix thoroughly, and when nearly cool add-

And when quite cold-

This mixture rapidly removes the vat blue, leaving only a whitish-grey. The pieces are then nearly dried, and winced first in a mixture of ground chalk and water, then in weak sulphuric acid sours, at 2° Tw., then in water. They are next well washed and dried, when the discharged portions will be found of a pure white. If the pieces have been exposed to sunlight after the chroming process, or dried too sharply at an elevated temperature, the blues are spoiled.

Indigo Greens, or Dipped Greens, are now in less request than formerly. In producing them either white cloth, or cloth printed and dyed with madder colours, is printed with No. 5 or 6 (Style V.) by block or machine as most appropriate. The green dipping is next effected as follows:—The pieces pass first through an ordinary light blue vat; then after travelling some yards in the air to secure oxidation, they enter a lead vat, composed of 250 lbs. brown sugar of lead and 130 lbs. of dry slaked lime, dissolved in 1000 gals. of water. They then enter a third vat of water alone, and pass finally through a vat of solution of bichrome, at 4° Tw., which brings up a yellow with the lead, and thus converts the blue into a green.

Seventh Style.-Discharges on Turkey-Reds.

No. 1. White Discharge (Machine) .-

Tartaric acid solution,	at 62°	Tw.	 	 	r gal.
Acetic acid, at 6° Tw.			 	 	I ,,
British gum (light)			 	 	8 lbs.

No. 2. White (Machine)	
Tartaric acid	6 lbs.
Water	r gal.
Starch	1½ lbs.
No. 3. White (Block)	
Tartaric acid	9 lbs.
	I gal.
Pipe-clay	
Gum Senegal water	3 quarts.
No. 4. White (Block).—	
Tartaric acid	Io lbs.
China clay	7½ ,,
Bichloride of tin	I ½
Gum water	I pint.
	I gal.
No. 4a. White.—	
Water	
Tartaric acid	15 lbs.
Dissolve at a boil, and beat up with—	
Pipe-clay	9 lbs.
And add—	
Gum water	} gal.
Containing 2 lbs. gum.	
No. 4b. White	
Water	
White starch	3 lbs.
Boil well together, and add-	
Tartaric acid	2
Oxalic acid	½ lb.
No. 5. Black Discharge	
Logwood liquor, at 4° Tw	I gal.
Yellow prussiate	
Gum-tragacanth water (thick)	I quart.
	2 lbs.
Boil and add—	
Iron liquor, at 30° Tw	2 quarts.
When cool add—	. *11
Nitrate of iron, at 80° Tw	I gill.
No. 5a. Black Discharge.—	
	I quarts.
, 0	1½ ,,
	3½ ozs.
Boil well together, and add—	
Bleu de Paris, dry	I2 ozs.
Previously stirred up with hydrochloric acid.	
	2 Q :

596 DYEING AND CALICO PRINT.	ING.
No. 6. Blue-black Discharge	
Logwood liquor, at 8° Tw	3 gals.
Gall liquor, at 9° Tw	
G. 1	20 lbs.
Boil and add whilst still hot—	
Yellow prussiate	2½ lbs.
When cold add—	
Muriate of iron, at 60° Tw	3 quarts.
Nitrate of iron, at 80° Tw	3 "
No. 7. Black.—	
Logwood liquor, at 8° Tw	7 gals.
Pyroligneous acid	I gal.
Starch	to lbs.
Boil and add—	
Copperas	2 lbs. 10 ozs.
Boil again, cool, and add—	
Nitrate of iron, at 80°	5 - 1
Blue paste (see below)	I gal.
No. 8. Blue Paste.—	
a. Copperas	
Water	
b. Prussiate of potash	
	I gal.
Mix a and b together, and add—	
Standard red liquor	I quart,
Nitric acid, at 60° Tw	I quart.
No. 9. Blue Discharge (Machine).—	**
a. Prussian blue	
Oxalic acid	
Hot water	
b. Water	
Starch	
Boil and add—	
Tartaric acid	2 lbs.
Mix a and b together.	
No. 10. Blue Discharge	
Tartaric acid	5 lbs.
	I gal.
Tin pulp	і "
Double muriate, at 120° Tw	
Gum tragacanth water	2 ,,
No. 11. Blue Discharge,-	
Oxalic acid	8 ozs.
	4½ lbs.
Yellow prussiate	2 ,,
Copperas	2 OZS.
Starch	r lb.
Gum tragacanth	2 OZS.
Water	3 quarts.

	331
No. II a. Blue	
Water	gal.
Tragacanth mucilage	19
Citric acid	lbs.
	3 1,
	1/2 ",
Boil well together, and add to the mixture when cold—	
* *	lb. 11 ozs.
No. 12. Yellow Discharge (Block).—	
	gal.
·	lbs.
	11
When dissolved add—	
, , , , , , , , , , , , , , , , , , , ,	lbs.
Gum Senegal	23
No. 13. Yellow Discharge (Machine) As No. 12, but instead	ad of China
clay and gum thicken with 1½ lbs. starch.	
No. 14. Yellow Discharge (Machine)	
	gal.
	i lbs.
	11
	1 ,,
Boil, and add when cool—	
	lb. 14 ozs.
No. 15. Yellow (Machine)	
	gals.
	lbs.
Boil, and add—	,
Nitrate of lead	bs.
Tartaric acid 15	
No. 16. Yellow (Machine).—	
Lime-juice, at 18° Tw	701a
Nitrate of lead 8	
Tartaric acid	
Gum substitute 6	
No. 16 a. Yellow.—	73
	ha
Pipe-clay	
	0.5
Boil up and incorporate thoroughly: then add-	gal.
Boil up and incorporate thoroughly; then add—	
Tartaric acid 81	bs.
Tartaric acid	bs.
Tartaric acid 81	bs.
Tartaric acid	bs. ,, gal.
Tartaric acid	bs. ,, gal.
Tartaric acid	bs. gal.

No.	16 b. Ye	ellow.										
	Tragac	anth	muc	ilage								rl gal.
		(3)	gals.	water	r to	2 lbs.	gui	n tra	agac	anth.	.)	
	White	starc	h									6 lbs.
	Water											₹ gal.

Any of these discharges, as may be required, is printed in, and when dry the pieces are run through the "decolouring vat," which is composed as follows:—

Stir well, till quite free from lumps and coarse fragments. A frame, with wooden rollers at top and bottom, is then set in the liquid, which is kept constantly stirred up, so as to be perfectly homogeneous. The pieces are then run through the liquid at the rate of one (28 yards) in three minutes. After passing through the squeezing-rollers they are passed into water and rinsed, and then winced for ten minutes in solution of bichrome, at 4° Tw. They are next washed in pure water, and again in water soured with muriatic acid; washed again, and dried. Except where the discharges have been printed on, the Turkey red is not perceptibly affected, but in those places it is discharged the design either remains white, or a mineral colour—blue, yellow, green, &c.—is left in place of the red.

Eighth Style .- Steam Colours.

This style embraces those colours which are developed and fixed by steam. The experiments which first led to the adoption of this process were made with dry heat. As these attempts were unsatisfactory, steam was introduced, though it was at first apprehended that the colours would run. Its action is simply that of heat combined with moisture, both being regular and under control. The modes of steaming vary greatly in different establishments. In some works, before steaming, the pieces are exposed to the air, at common temperatures, for a day and a night; whilst in others the calico goes direct from the machine to the steam-chest. The degree of moisture in the steam varies also greatly, some practical men using it very dry, and others damp, being of course guided by the quality of the goods, the nature of the colours

and thickening, and the effect to be produced. In some establishments the steam is applied for a short time, when the goods are taken out, exposed to the air, and steamed again. In others the goods are exposed to the action of the steam for the required time without interval. The two principal contrivances for steaming are the "column" and the "chest," each of which has its advocates. The column is a cylinder of copper, about 44 inches in length, and varying in diameter from 3 to 5 inches, its surface pierced all over with small apertures, Tath of an inch in diameter and set 1th of an inch apart. Around this cylinder the goods are coiled, a copper plate, of about 9 inches in diameter, being soldered to its bottom end, to prevent the cloth from slipping off. At the lower end of the column is fixed a pipe, with a tap to regulate the entrance of steam from a boiler. There are various arrangements for the admission of the steam and for the exit of condensed water. The cylinder is enfolded first in several layers of a woollen tissue, then in several folds of white calico, and lastly in the printed goods. It is then enclosed in a wrapping of white calico. The steaming is kept up for twenty to thirty minutes, according to the nature of the dye. As soon as the steam is shut off the pieces are unrolled, to prevent the running of the colours in consequence of the condensation of steam.

The steam-chest, however, is the apparatus most generally employed in this country. It is an iron chamber with a pent-house top, usually about 12 feet long, 6 wide, and 9 high at the top. At one end it is fitted with a closely-made folding-door, secured with a cross bar, held in its place by screws. The chest has a false bottom on a level with the floor of the room. Beneath this runs a steam-pipe perforated with holes, and extending under three sides of the chest. The steam escapes through the holes in this pipe, and is distributed still more completely by means of the holes in the false bottom. Upon this false bottom are placed two rails, parallel with the sides of the chest, and extending beyond the chest into the room. The part of these rails nearest the chest, for a feet, is fitted with hinges, so as to be movable on one side when the door is opened or shut. An oblong frame of wood moves upon these rails, fitting closely inside the chest, and standing as high as where the slope of the roof begins. When this frame has been drawn out into the room it is filled with pieces as follows:-They are wound one after another upon an open reel, keeping the selvages of each fold parallel. Each piece is then drawn off the end of the reel and flattened, when a thread is passed through all the selvages of one side, and loops are made through which pass wooden rods that are supported on the sides of the carriage. The pieces now.hang with their selvages downwards, and the carriage, which is fitted with rods, slides back into the steam-chest, when the doors are shut, and the steam escapes by a safety-valve. After exposure for three-quarters of an hour the pieces are taken out, unfolded, and again loosely folded, to be ready for rinsing off. They are then stitched together, end to end, and passed through a cistern containing water, and thence into another filled with a very dilute solution of red chrome. They are next washed in the machine, transferred to the hydroextractor, starched, and dried.

This style of printing has a considerable resemblance to woollen and worsted dyeing, since some of the mordants are applied simultaneously with the extracts of dye-woods, or other colouring matter, both being, in fact,

incorporated with each other. After this mixture has been printed on the calico, the action of the steam, like that of boiling water in woollen-dyeing, effects the combination between mordant, colour, and fibre. The finest effects in this style are obtained by preparing the cloth first with a tin mordant, so as to fix peroxide of tin in the fibre. In case of woollen and worsted goods, indeed, this "preparing," as the operation is technically called, is absolutely necessary for the production of good colours. The peroxide of tin thus deposited in the fibre acts not only as a mordant, but it helps in neutralising the acidity of many steam-colours, and aids thus in the formation of sub-salts—or basic compounds—which combine most readily with colouring matters. The methods of "preparing" in different print-works vary greatly, according to the judgment of the proprietor, the kind of cloth operated upon, and the effects intended to be produced. The article generally used is, however, the stannate of soda, often known in the trade, in consequence, as "alkaline preparing salts."

Calicoes are frequently prepared as follows:—The pieces, stitched together by their ends, are padded, with a machine with wooden rollers, in a solution of stannate, at 10° Tw. This process is repeated twice, with the interval of an hour, during which the pieces are allowed to remain wet. They are then winced through diluted sulphuric acid, at 1½° to 3° Tw.; winced again in pure water, and washed. The washing must be merely sufficient to remove free sulphuric acid. After this operation the pieces are unstitched, freed from excess of water in the hydro-extractor, and carefully dried at a steam-heat.

As a prepare for heavy shades the following procedure is in use:—The pieces are padded in stannate, at 24° Tw.; left wet for about two hours; winced in dilute sulphuric acid (technically called "vitriol sours"), at 6° Tw.; washed and partially dried in the hydro-extractor. These operations are all repeated once more, in the same order, and the pieces are then dried. The acid liquid, of course, soon becomes reduced in strength, from the amount of alkali neutralised—a point which requires constant attention, since, if the "sours" be not kept up to the proper pitch, the tin deposited on the fibre will wash off, and the work will be quite irregular.

Some printers use, along with the stannate of soda, arsenical compounds, and also the tungstate of soda. See chapter on Mordants, pp. 534 and 542.

The following steam-colours are in common use:-

N	o. I.	Steam-	$Black,$ $_{\square}$	for Cy.	lina	ler-worl	₹
---	-------	--------	-----------------------	---------	------	----------	---

Logwood extract, at 12° Tw.	 	 . I gal.
Gall liquor, at 9° Tw	 	 . I quart
Mordant (see below)	 	 . r ,,
Flour	 	 . 2 lbs.
Starch	 	 6 ozs.

The whole is boiled for ten minutes, and mixed with ½ pint nitrate of iron.

The mordant above mentioned consists of—

Acetic acid	 	 	 	I quart
Acetate of copper				-
Iron liquor, at 24° Tw.	 	 	 	I 1 ,,
Red liquor, at 20° Tw.	 	 	 	ı quart.

No. 2. Another Black.
Logwood liquor, at 6° Tw I gal.
Starch 1½ lbs.
Boil, and add whilst still hot-
Copperas 5 ozs.
Stir thoroughly, and when the mixture is almost cold add-
Gallipoli oil
Nitrate of iron, "well killed" 10,,
No. 2 a. Black.—
Logwood liquor, at 12° Tw I gal,
Gall liquor, at 9° Tw
Red liquor, at 20° Tw I
Iron liquor, at 24° Tw
Acetic acid
Thicken with—
Wheat flour
Starch
Boil, and add—
Gallipoli oil , r pint
Oil of turpentine
This colour is useful either for steaming, raising through soda and washing of
in water, or for a black to work with garancin or alizarin purple to go through
the dye-beck.
No. 3. Blue, for Cylinder, Dark
Water 7 gals.
Starch
Sal-ammoniac
Boil these ingredients, and whilst hot add—
Yellow prussiate, ground 12 lbs.
Red prussiate 6 ,, Tartaric acid
,,,
When the mixture is nearly cold add—
Sulphuric acid, at full strength
Oxalic acid (previously dissolved in 2 lbs. hot water) 2 lbs. Tin pulp (see below) 6 gals.
The tin pulp just mentioned is prepared as follows:—Take the strongest
double muriate of tin (solution of protochloride of tin), and add as much
solution of yellow prussiate as will throw down all the tin as a ferrocyanide.

solution of yellow prussiate as will throw down all the tin as a ferrocyanide. This precipitate is washed in pure water by decantation, and drained on a filter till it becomes a stiff paste.

No. 4. Another Dark Bli	ie.				
Water		 	 	 	 8 quarts
Yellow prussiate					
British gum (nale)					

Boil, and add—
Bisulphate of potash
Sal-ammoniac
Alum
Oxalic acid
Sulphuric acid, at 170° Tw
Tin pulp r gal.
No. 5. Light Blue for Cylinder.—
Dark blue, No. 3 4 quarts.
Gum substitute water (4 lbs.) 12 ,,
No. 6. Blue Standard.—
Water
Alum
Oxalic acid 4½ ozs.
Yellow prussiate
Gum substitute water 4 quarts.
No. 7. Another Blue Standard, Common.—
Water 8 quarts
Yellow prussiate 4 lbs.
Alum 3 lb.
Sulphuric acid, at 170° Tw
No. 8. Another Blue.—
Water 12 quarts
Starch 4 lbs.
After boiling add—
Sal-ammoniac
Tartaric acid
Tin pulp 4 quarts.
No. 9. Another Blue.—
Water 4 quarts
Starch
Boil, and add —
Oxalic acid 10 ozs.
Tartaric acid
Yellow prussiate 3½,
When all is thoroughly dissolved and incorporated, and the mixture is grown
cold, add—
Sulphuric acid, at 170° Tw 8 ozs.
Tin pulp r pint.
No. 10. Common Blue.—
Gum water 2 quarts
Blue standard (No. 7) quart.
Add a little extract of indigo to "sighten." For patterns of steam-blues see
pp. 164 and 165.

No. II. Brown.—
Berry liquor, at 20° Tw 1½ gal.
Brazil-wood liquor, at 8° Tw
Alum 3 lbs.
Lavender liquor (see below)
Gum Senegal water (6 lbs.)
Nitrate of copper, at 100° Tw
* * '
No. 12. Lavender Liquor.—
Red liquor, at 18° Tw 2 gals.
Logwood, ground 6 lbs.
Let steep for forty-eight hours, and strain off the clear liquor. Some makers
boil the mixture instead of steeping in the cold. A stronger liquor is made
with 10 lbs, of ground logwood to the same amount of red liquor.
No. 13. Brown Standard.—
Bark liquor, at 12° Tw 14 quarts
Sapan liquor, at 12° Tw 3½ ,,
Logwood liquor, at 12° Tw
Gum substitute water (8 lbs.) 12 ,,
Alum
Chlorate of potash 2 ozs.
Red prussiate 5 ,,
From this shades of light brown are made by reducing with gum-water.
No. 14. Another Brown.—
Bark liquor, at 12° Tw 3 quarts
Sapan liquor, at 10° Tw 2 ,,
Berry liquor, at 12° Tw 3 ,,
Logwood liquor, at 12° Tw 2 ,,
British gum
Boil, and add
Alum
Sal-ammoniac
Blue vitriol 8 ,,
Nitrate of copper, at 80° Tw ½ pint
Lilac standard (see below) 3 quarts.
,
No. 15. Lilac Standard.— Logwood liquor, at 20° Tw 4 quarts.
Heat it to 175°, and dissolve in it—
Alum
Oxane acra 11 11
Binoxalate of potash 2 ozs.
No. 16. Another Brown.—
Berry liquor, at 3° Tw 4 quarts
Peachwood liquor, at 8° Tw 2 ,,
Logwood liquor, at 8° Tw
Nitrate of copper, solid 1½ lbs.
Alum



STANDARD BROWN (LIGHT).

No. 16 a. Light Brown.

Brown standard (see ne	ext	age)			 		I gal.
Gum-water (4 lbs.)		* *			 		I ,,
Acetate of alumina, at	18°	Tw.			 		I pint
Nitrate of copper			٠		 		I quart.

Mix well. When printed, age and let lie four nights, and pass through dilute arseniate of soda, at 180° F. Wash with hot water, and run through very dilute chloride of lime on the mangle, dry, and finish.

No. 16 b. Dark Brown.—Same colour as No. 16 a. When printed, steam thirty minutes, age two nights, wash off in weak solution of bichrome; wash well, dry, and finish.



STANDARD BROWN (DARK).

No. 16c. Brown Standard, referred	l to in	n Nos	s. 16	a ar	nd b.	
Catechu, cubic						
Water			* <			8 gals.
Boil eight hours, and add-						
Acetic acid						2½ quarts
Then dissolve—						
Sal-ammoniac						rolbs.
In-Water						1½ gals.
Mix both liquids well; let settle, and	thick	en th	e cle	ar li	quor	with gum-water.
No. 17. Buff (Chamois).—						
Madder liquor						3 gals.
Bark liquor, at 10° Tw						4 quarts
Red liquor, at 14° Tw						2 gals.
Starch						7 lbs.
Boil, and add—						,
						2 OZS.
No. 18. Chocolate (for Cylinder-W						2 0201
Logwood liquor, at 12° Tw.						a gala
Sapan liquor, at 12° Tw			• •	• •	• •	3 gals.
* *				• •		2 ,,
Nitrate of alumina (see below		• •	• •	• •	• •	ı gal.
Bark liquor, at 12° Tw			• •		• •	1 ,,
Water				4 +		4 gals.
Starch		* *		• •	• •	17 lbs.
Boil, and then add—						
Chlorate of potash				• •	• •	½ lb.
Red prussiate		• •	• •	• •	• •	2½ lbs.
No. 19. Nitrate of Alumina						
Boiling water						8 gals.
Nitrate of lead, crystals						24 lbs.
Alum		0.0	* *			24 ,,
Carbonate of soda, crystals						5 "
Stir till dissolved; let settle, and draw	off :	the cl	lear	liqui	d for	use.
No. 20. Another Chocolate						
Sapan liquor, at 9° Tw						12 quarts
Nitrate of alumina						3 ,,
Logwood liquor, at 12° Tw						6 ,,
Yellow prussiate						6 ozs.
Red prussiate						6 ,,
Chlorate of potash						6 ,,
Starch						g lbs.
This formula requires well boiling and						9 103.
	*****	**6'				
No. 21. Another Chocolate.—						1
Sapan liquor, at 8° Tw.			* *			5 gals.
Red liquor, at 16° Tw.			* *	* *	• •	6 quarts
Nitrate of alumina						6 ,,
Logwood liquor, at 18° Tw.		• •			* *	2 gals.
Bark liquor, at 18° Tw.	n' e		***			3 quarts
Starch	4.4			4.0		16 lbs.

D 11 1 11 1						
Boil, and add when cold—						
Red prussiate						ı lb.
	• • • • •			• •	* *	2 lbs.
_			• •	• •		2 ,,
These receipts admit of almost inf	hnite v	ariatio	ons.			
No. 22. Cinnamon						
Cochineal liquor, at 8° Tw						1 quart
Logwood liquor, at 8° Tw						I ,,
Berry liquor, at 10° Tw.						ı ,,
Alum						б ozs.
Cream of tartar						4 ,,
Starch						8 ,,
Boil, and add whilst still warm—						
Tin crystals (protochloride)					* *	3 ozs.
No. 23. Drab.—						
Lavender liquor						4 gals.
						4 ,,
Bark liquor, at 8° Tw						r gal.
Gum-water, from 40 to 70 g	gals.					
No. 24. Dark Drab.—						
'						4 quarts
Gum-substitute						7 lbs.
Boil and cool, and next add—		• •				/ 103.
Alum						24 OZS.
Copperas						16 ,,
Logwood liquor, at 2° Tw.						ı quart
Cochineal liquor, at 3° Tw						I ,,
			• •		• •	- "
No. 25. Another Drab.						
Boiling water		• •	• •	* *	* *	3 quarts
			• •			I pints
Bark liquor, at 30° Tw. Yellow prussiate (dissolved					• •	å pint I oz.
This mixture is thickened with gum				,	· ·	
		_				
No. 26. The Lilac Standard, abo						
Logwood liquor, at 12° Tw.						8 gals.
Red liquor, at 18° Tw		• •		* *		8 ,,
Oxalic acid					• •	4 lbs.
Sal-ammoniac					* *	5 "
Acetate of copper, crystallis	sed	* *		• •		21,,
No. 27. Green (for Cylinder-Wor	·k)					
Berry liquor, at 12° Tw.						7 gals.
						15 lbs.
						8 ,,
Gum-substitute						28 ,,
Boil, and add-						
					٠.	2 lbs.
Oxalic acid						2 11

No. 28. Green for Block-Work	
Hot water 6 gals.	
Yellow prussiate 28 lbs.	
Mix meantime in a separate vessel—	
Water	
Double muriate of tin, at 120° Tw I gal.	
Gum Senegal water (6 lbs.) 10 gals.	
Mix these two solutions by pouring backwards and forwards, and stirring v	erv
briskly. When the whole is perfectly incorporated and clear add—	0. 9
Berry liquor, at 10° Tw 12 gals.	
Tartaric acid	
Oxalic acid (dissolved in 5 gals. water) 2½,	
Acetic acid	
Extract of indigo	
No. 29. Green (inferior quality)	
Starch	
Bark liquor, at 16° Tw 8 gals.	
Boil, and add—	
Alum 3 lbs.	
Oxalic acid	
Tin crystals	
•	
When nearly cold add— Tartaric acid	
Tartaric acid	
Tin pulp	
No. 30. Green for Blotch Grounds	
Bark liquor, at 10° Tw 8 gals.	
Starch 12 lbs.	
Boil together, and add—	
Alum 5 lbs.	
Yellow prussiate, 12 ,,	
Tartaric acid 6 ,,	
Oxalic acid	
Tin pulp ½ gal.	
Steam-greens after printing are frequently brightened, or "raised" as it	t is

Steam-greens after printing are frequently brightened, or "raised" as it is technically called, by passing through a weak bath of bichrome.

No. 30 a. Aloes Green .-

Chrysammide (see p. 417) 2 grms.
Gum-water, according to shade.

After steaming, this mixture gives a fine moss-green, not affected by boiling water, or madder and garancin baths. Thus a variety of modifications can be produced. A design may be printed by this means in deep green; a green ground may be obtained. Iron and alumina mordants may then be printed on, and the pieces dyed in the madder or garancin beck. The result will then be—in the one case, a white ground, with green, red, purple, chocolate, and black figures; or, in the other case, a green ground with a design in the four latter colours, or any of them.

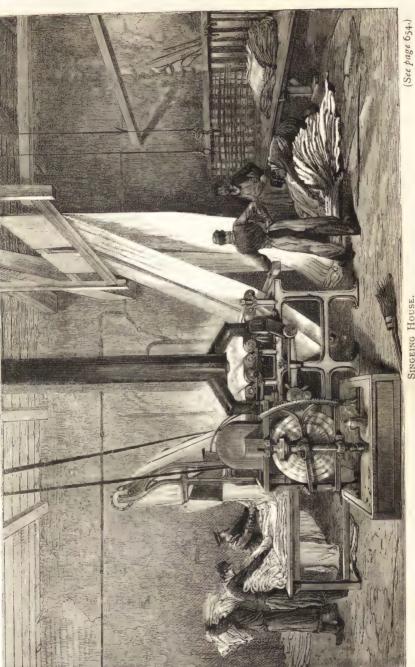
Gum-water 4 gals. Lilac standard, No. 26 2 ,, Yellow prussiate 4 lbs. Hot water 1 gal. No. 32. Lavender.— 4 gals. Lavender liquor, No. 12 4 gals. Blue standard, No. 6 4 ,, Gum-water (according to shade) 24 to 48 gals. No. 33. Lilac (Dark).— 6 gals. Purple standard (see below) 2 ,, Gum-substitute 20 lbs. No. 34. Lilac (Light).— 6 gals. Purple standard 6 gals. Purple standard 2 ,, Gum-water 6 ,
Yellow prussiate 4 lbs. Hot water 1 gal. No. 32. Lavender.— 4 gals. Lavender liquor, No. 12 4 gals. Blue standard, No. 6 4 " Gum-water (according to shade) 24 to 48 gals. No. 33. Lilac (Dark).— 6 gals. Purple standard (see below) 2 " Gum-substitute 20 lbs. No. 34. Lilac (Light).— 6 gals. Pink standard 6 gals. Purple standard 6 gals. Purple standard 2 "
Yellow prussiate 4 lbs. Hot water 1 gal. No. 32. Lavender.— 4 gals. Lavender liquor, No. 12 4 gals. Blue standard, No. 6 4 " Gum-water (according to shade) 24 to 48 gals. No. 33. Lilac (Dark).— 6 gals. Purple standard (see below) 2 " Gum-substitute 20 lbs. No. 34. Lilac (Light).— 6 gals. Pink standard 6 gals. Purple standard 6 gals. Purple standard 2 "
No. 32. Lavender.— Lavender liquor, No. 12
Lavender liquor, No. 12
Blue standard, No. 6
Blue standard, No. 6
Gum-water (according to shade)
Pink standard (see below)
No. 34. Lilac (Light).— Pink standard 6 gals. Purple standard
Pink standard 6 gals. Purple standard 2,,
Gum-water 6 ,,
No. 35. Pink Standard.—
Cochineal liquor, at 6° Tw 4 gals.
Alum 2 lbs.
Cream of tartar 2 ,,
Oxalic acid

This mixture, thickened with 4 gals. of thick gum Senegal water, forms a pink steam-colour. The proportions of alum, cream of tartar, and oxalic acid used by different printers vary considerably, some putting, to the above quantity of cochineal liquor, only 1½ lbs. alum, 12 ozs. cream of tartar, and 4 ozs. of oxalic acid, whilst others employ intermediate quantities.

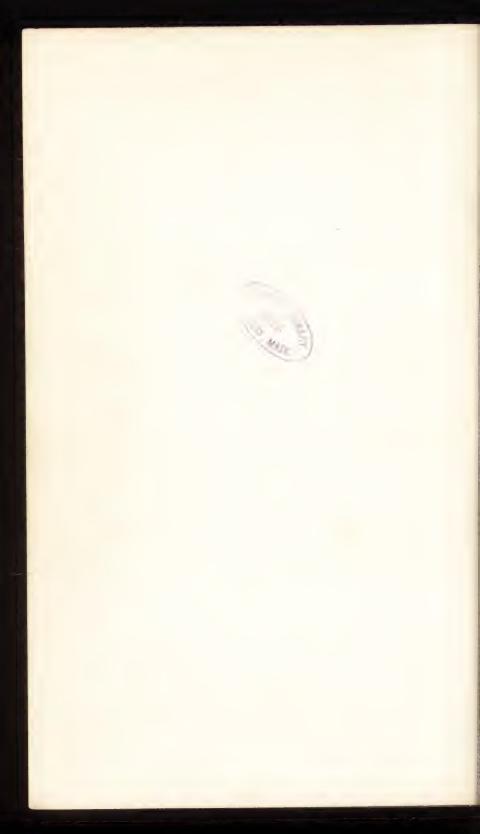
No. 36. Purple Stand	ard.		
Logwood liquor,	at 12° Tw.	 	2 gals.
Alum		 :	12 ozs.
Red prussiate		 	8 ,,
Oxalic acid		 	4 ,,

This quantity, mixed with 8 gals. gum substitute water, forms a good cylinder colour. If wanted for block-printing, 12 gallons of gum-water are required. Here, also, the amount of salts and acids varies in different establishments. In some receipts, to 2 gals. of logwood liquor, 1 lb. of red prussiate, 1½ lbs. alum, 2 ozs. of oxalic acid, and 4 ozs. of oxalate of potash are used.

No. 37. Pink (Sag	ban Woo	d)	-				
Sapan liquo	r, at 3° I	·w.		 	 	 	2 gals.
Pink salt				 	 	 	2 lbs.
Sal-ammoni	ac			 	 	 	ı lb.
Oxalic acid				 	 	 	2 ozs.
Sulphate of	copper			 	 	 	2 ,,
Gum-water	(thick)			 	 	 	2 gals.

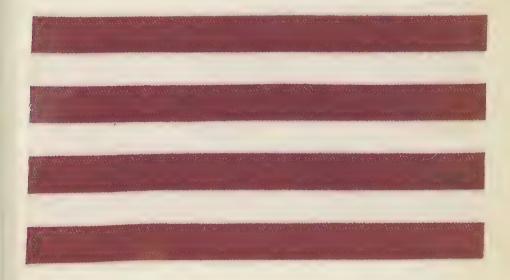


SINGEING HOUSE.



No. 38. Pink (Sapan and Cochineal mixed).—										
Sapan liquor, at 8° Tw	5 gals.									
Cochineal liquor, at 8° Tw	ı gal.									
Nitrate of alumina										
Alum										
Oxalic acid										
Chlorate of potash	8 ,,									
After the other ingredients are incorporated there is added—										
Gum water	12 gals.									
No. 39. Pink (Cochineal).—										
Cochineal liquor, at 6° Tw	2 gals.									
Heat to about 168° F., and dissolve—										
Alum ',	I2 ozs.									
Cream of tartar	6 ,,									
Oxalic acid	I oz.									

This colour is mixed with various amounts of gum-water, according to the shades required. For other cochineal pinks, crimsons and reds, &c., see under "Cochineal."



COCHINEAL PINK.

No. 39 a. Cochineal Pink.

	Cochineal liquor, at 8° Tw.	0.5	9.8				I gal.
	Starch	• •	• •	• •	• •	• •	I 1 lbs.
Boil	a little, and add-						
	Oxalic acid		• •		• •	• •	3 ozs.
Diss	solve, and strain for printing. Who	en p	rinte	đ, ste	eam	forty	minutes at 3 lbs.
ores	sure; let lie one night; run throug	gh a	very	dilu	te so	olutio	n of alum on the
mar	gle, and finish.						

DYEING AND CALICO PRINTING.	
No. 40. Purple, Ordinary.	
Logwood liquor, at 10° Tw 6 gals	
Red liquor, at 18° Tw.	1 0
In which latter dissolve separately—	
Carbonate of soda, crystals 1½ lb	
Oxalic acid	,
When all is dissolved add—	
Gum Senegal, in powder 36 lbs	•
No. 41. Purple, Decp.—	
Logwood liquor, at 16° Tw 1 gal.	
Red liquor, at 20° Tw ,,	
Soda crystals 4 ozs.	
Red prussiate	
Oxalic acid	
Gum Senegal 6} lbs	
	•
No. 42. Red, Dark (for Cylinder).—	
Sapan liquor, at 12° Tw 2 gals	i.
Bark liquor, at 8° Tw ½ gal	
Nitrate of alumina	
Chlorate of potash 4 ozs.	
Alum	
Starch 61/2 ,,	
Gum substitute 1lb.	
No. 43. Red.—	
Sapan liquor, at 10° Tw 4 gals	
Bark liquor, at 18° Tw 14 qu	
Red liquor, at 20° Tw	
Alum	· .
Chloride of copper (crystals) 12½ oz	s.
No. 44. Red.—	
Sapan liquor, at 8° Tw 2 gals	
Nitrate of alumina 11 ,	
Alum	
Chlorate of potash 2½ 07	
Starch 33 lbs	
No. 44 a. Corallin Red.—	
Corallin roo grm	S.
Alcohol	
Dissolve, and add—	
Solution of casein	c
To prepare this solution take—	٥.
* *	c
	3.
Water	
Ammonia 20 ,,	-1k-11
Others add oxide of zinc to the above mixture, or mix intimately the	
solution of corallin with oxide of zinc, and thicken with albumen.	Or the

solution of corallin may be mixed with magnesia and oxide of zinc, and thickened either with albumen or with glycerin and gum-water.

No. 44 b.—Aloes, Rose.
Gum-water
This mixture, without steaming, produces a rose on cotton, silk, or wool. The
shades resist washing, and are not modified if the pieces have been prepared
with stannate of soda. On steaming, the rose is converted into a violet.
No. 44 c. Deep Red (Artificial Alizarin)
Alizarin paste, at 15 per cent 800 grms.
Acetic acid, at 6° Baumé Ilitre
Water 2 litres
Olive oil
Acetate of lime, at 10° Baumé 200 ,,
Wheat starch 500 ,,
Boil well, stir till cool, and incorporate—
Acetate of alumina 200 grms.
No. 44 d. Rose-Colour.—
Alizarin paste, at 15 per cent 1600 grms.
Thickening for reds 8 litres
Acetate of alumina, at 12° Baumé 500 grms.
Acetate of lime, at 16° Baumé 250 ,,
The paler the shade required the more thickening must be used. (See also
p. 225).
No 15 Stone-Colour
No. 45. Stone-Colour.—
Lavender liquor, No. 12 4 gals.
Lavender liquor, No. 12 4 gals. Blue standard, No. 6 6 ,,
Lavender liquor, No. 12 4 gals. Blue standard, No. 6 6 ., Bark liquor, at 12° Tw
Lavender liquor, No. 12 4 gals. Blue standard, No. 6 6 ,,
Lavender liquor, No. 12 4 gals. Blue standard, No. 6 6 ., Bark liquor, at 12° Tw
Lavender liquor, No. 12
Lavender liquor, No. 12 4 gals. Blue standard, No. 6 6 ., Bark liquor, at 12° Tw
Lavender liquor, No. 12



PALE YELLOW FROM PERSIAN BERRIES.

No. 49. Dar	k Yellor	w								
Berry 1	iquor, a	t 4° T	w							r gal.
Flour	* 4									I lbs.
Boil, and add-										
Alum.										g ozs.
When cool add—										
Tin cry	ystals		* •							3 ozs.
When dissolved	l, strain	. Aft	er pr	intin	g, ste	am fo	r thi	rty n	ninut	es, as in No. 48

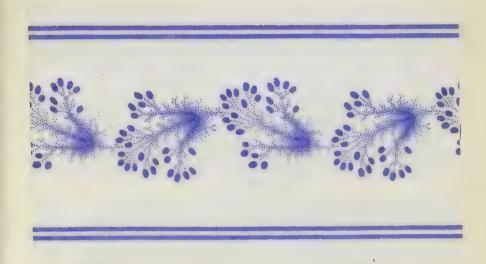


DARK YELLOW FROM PERSIAN BERRIES.

For other patterns, and particulars of various coal-tar colours fixed by the steam process, the reader is referred to pp. 206, 207, 217, 218, 225, and 226.

Hofmann Violet on Calico.

The colour is mixed with red liquor, and with a solution of arsenious acid in water to which some glycerin has been added, as directed on p. 207. Both these compounds together form the mordant. After steaming for an hour it is gently soaped. The colour is thickened with gum and starch.



HOFMANN VIOLET.

Delaines.

The method of printing delaines, and other mixed fabrics composed of wool, or worsted, with a cotton warp, may be treated as an appendix to the steam style. The preparation of the goods is different, and in most cases the colours are mixed differently, so as to be suitable both for the cotton and wool. The steaming and subsequent operations are very similar to those recommended for calico. The first step is the bleaching of the goods, which is exceedingly important, and which is performed by means of the fumes of burning sulphur. For this purpose they are hung up in a close brick or stone chamber, and sulphur, being placed upon the floor in iron dishes, is set fire to, and the door is tightly closed. After the lapse of some hours the pieces are taken out and washed. The following improved apparatus (Figs. 37 and 38) is the invention of Mr. John Thom.

A (Fig 37) represents the roof of the chamber, made of sheet-lead, of 4 lbs. to the square foot. B is a lead pipe, of I inch diameter, to carry off any excess of sulphurous gas. C c are rolls of pieces, to enter the chamber at one side and come out at the other. DD are wooden cylinders, turning on iron axles. EE represents the flooring, made of perforated tiles, similar to the floor of a malt-kiln, through which the sulphurous acid gas enters.

Fig. 38 represents the sulphur-chamber, 6 feet long by 4 broad and 5 high, 1 fitted with two windows, placed opposite to each other. F is an iron tray in

which the sulphur is burned, placed on a sloping flag-stone, inclined to the chamber at 1 inch in the foot. There is a slide by which fresh supplies of sulphur may be introduced, and air admitted, as required. The air-opening is

FIG. 37.

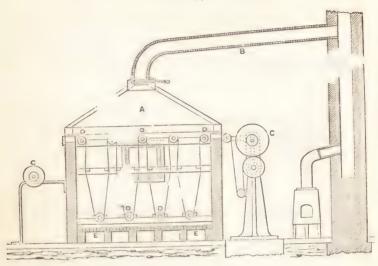
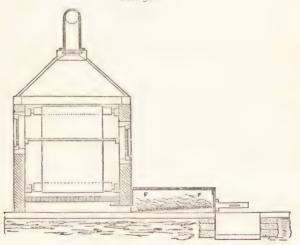


Fig. 38.



from an inch to r inch. Delaines, as well as goods consisting entirely of wool or of worsted, are sometimes bleached by means of concentrated solutions of the bisulphites of soda or of magnesia.

The preparing, which is the next step, is also of capital importance. The pieces are generally padded twice, by means of a machine with wooden rollers, in stannate of soda. Next they are run through water mixed with sulphuric acid and marking 3° Tw., gently washed and partly dried, and, lastly, they are twice padded in dilute sulpho-muriate of tin, at about 4° Tw. Some printers, however, prepare delaines like calico, by merely padding in stannate, souring, &c., as described on p. 600. Others use a variety of "prepares." Thus the pieces are padded four times, in a solution formed of equal parts of bichloride of tin, at 120° Tw., and double muriate of tin (protochloride), at 120° Tw., and let down with water to 10° Tw.; then in dilute sulphuric acid, at 4° Tw.; then in chloride of lime, at 0.5° Tw., washed, placed in the hydro-extractor, and dried. Whatever be the "prepare," it is advisable to pass the pieces from it, without washing, directly into the weak solution of chloride of lime just mentioned, after which they are washed and dried.

The solution of sulpho-muriate of tin above mentioned is prepared by mixing-

Mix together very gradually, and add-

Muriatic acid 4 quarts.

For use, reduce with water to 4° Tw. When the pieces, after preparing, are ready for printing, they are padded in weak gum Senegal water (\frac{1}{2} lb. per gallon), and dried.

The following are some of the colours ordinarily used for printing delaines:-

No. I. Black .-

Logwood liquor, at r2° Tw. 3 gals. Starch 3 lbs.

Boil well together, and when the mixture has cooled to about 88° to 90° F. add-

No. 2. Black .-

Pyroligneous acid, at 7° Tw... I quart.

r lb.

No. 3. Blue, Dark or Royal .-

 Water
 6 gals.

 Starch
 6 ½ lbs.

Sal-ammoniac 21 lbs.

Boil the whole well and add-	
Tin pulp 6 gals.	
Stir and mix well in, and add—	
Yellow prussiate, ground 16 lbs.	
Red prussiate 8 ,,	
Tartaric acid 24 ,,	
Oxalic acid (dissolved in 2 quarts hot water) 11,	
No. 4. Medium Blue.—	
Standard blue (No. 6) 6 gals.	
Oxymuriate of tin, at 120° Tw 1½ quarts.	
The latter ingredient is added gradually, and the mixture very well stirred	
Extract of indigo 21 quarts.	
No. 5. Blue, Pale.—	
Dark blue colour, No. 3	
Gum water 7 gals.	
For blotch- or ground-blues the proportion of gum-water is doubled.	
No. 6. Standard Blue.—	
Yellow prussiate	
A	
Alum 3 ,,	
Oxalic acid 2 ,,	
Water 4 gals. Gum-water (6 lbs. to the gallon) 4 ,,	
No. 7. Royal Blue.—	
Water ., 4 gals.	
Starch	
Solution of red prussiate, at 30° Tw 4 gals.	
Gum tragacanth water 2 quarts.	
Boil and add—	
Tin pulp	
Tartaric acid	
Oxalic acid	
Yellow prussiate	
*	
Tartaric acid	
No. 8. Blue, Dark Blotch.—	
Water 7 gals.	
Starch 8 lbs.	
Solution of red prussiate, at 30° Tw 3 gals.	
Solution of gum tragacanth 3 quarts.	
Boil the mixture, and add while still hot.	
Tin pulp 3 gals.	
Tartaric acid	
Oxalic acid	
When cold add the clear liquid from the following mixture:— Prussiate of potash	
Tartaric acid	
Hot water 5 gals.	

No. 9	. Buff Standard.—	
	Cochineal liquor, at 8° Tw	r quart.
	Berry liquor, at 10° Tw	3½ quarts
	Red liquor, No. 41	I quart.
	Oxalic acid	20 OZS.
Gum-wa	ater is added according to the shades required.	
NY	. D #	
No. I	o. Buff.— Catechu liquor, ½ lb. per gallon	w 0110040
		5 quarts. 8 ozs.
To! I		o uzs.
Dissolve		
	Hot water	I quart.
	Acetate of copper	3 ozs.
	Nitrate of copper	10 ,,
Thicken	with gum-water according to shade.	
Ma =	I. Dark Brown.—	
140. 1	Sapan liquor, at 8° Tw	21 quarts
	Logwood liquor, at 12° Tw	I pint.
	Bark liquor, at 10° Tw	5 quarts.
	Alum	I2 ozs.
	Chlorate of potash	I OZ.
	Gum-substitute	6 lbs.
Boil and		
Don and		
	Red prussiate	4 ozs.
	Oxalic acid	2 ,,
No. 1	2. Pale Browns Reduce No. 11 with gum-water.	
NT		
No. 1	Berry liquor, at 8° Tw	5 quarts.
	Alum	1½ lbs.
	Orchil liquor, at 8° Tw.	I quart.
•	Sapan liquor, at 8° Tw	I pint.
	Logwood liquor, at 10° Tw	1 ,,
	Starch	ı lb.
Boil and		
Don and		
	Oxalic acid	2 OZS.
No. I	4. Brazil-wood Brown.—	
	Brazil- or peach-wood liquor, at 9° Tw	I gal.
	Berry liquor, at 18° Tw	I ,,
	Orchil liquor, at 12° Tw	$\frac{1}{2}$,,
	Starch	2 lbs.
Boil and	l add—	
	Alum	Il lbs.
	Sal-ammoniac	4 OZS.
	Acetate of copper	2 ,,

No. 15. Chocolate, Dark						
Sapan liquor, at 11° Tv	v					 2 quarts.
Bark liquor, at 14° Two						 l pint.
Logwood liquor, at 14°						 3 ,,
Gum						 3 lbs.
Alum						 12 ozs.
Chloride of copper (cr						 8 ,,
Sal-ammoniac						 21,,
						 -2 11
No. 16. Chocolate, Dark.						
Sapan liquor, at 8° Tw						 5 gals.
Red liquor, at 16° Tw.						$1\frac{1}{2}$,,
Logwood liquor, at 10°						 2 ,,
Nitrate of alumina						 I ½ ,:
Bark liquor, at 18° Two						 3 quarts.
Starch			• •		٠.	 15 lbs.
Boil, and when nearly cold add-						
Red prussiate of potas	h					 8 ozs.
Yellow prussiate						 ılb.
Chlorate of potash						 I ,,
No za Chandata						
No. 17. Chocolate.—						1 .
Sapan liquor, at 30° T				• •	• •	2 gals.
Red liquor, at 24° Tw.		• •				 2 ,,
Acetic acid (weak)						 I pint.
Starch						6 lbs.
Gum-substitute		• •				 8 ,,
Boil, and add—						
Alum						 1 lb.
Dissolved in-						
Logwood liquor, at 30	Tw					 3 pints.
Bark liquor, at 30° Tw	7					 ı quart.
Then add-						
Chlorate of potash						 2 lbs.
Dissolved in—						 2 103.
Gum tragacanth water						3 quarts.
Sal-ammoniac				0.0		ı lb.
Sulphate of copper						 6 ozs.
No. 18. Chocolate.—						
Sapan liquor, at 20° T	w					 2 quarts.
Nitrate of alumina						 2 ,,
Bark liquor, at 30° Tw						 r pint.
Logwood liquor, at 30						 ra pints.
						 7 lbs.
Chlorate of potash						5 ozs.
Dissolved in—						
Boiling water						 11 quarts.
Sulphate of copper						 I duarts.
outpitute of copper is						 1 2 020.

No. 19. Cinnamon (Block)							
Bark liquor, at 20° Tw.							2 gals.
Cochineal, ground							2 lbs.
Digest at a gentle heat, strain, an	d thi						2
Gum Senegal							7 1bs.
Extract of indigo							6 ozs.
Tin crystals							18 ,,
			• •				10 ,,
No. 20. Dove Colour.	,						
Dove blue (see below, No						• •	6 quarts
Lavender liquor (see No.					,		4 11
Gum Senegal water (6 lb	s. per	r gai	.)	• •	0 0		8 ,,
No. 21. Dove Blue							
Water			* *	* *			5 quarts.
Yellow prussiate							2 lbs.
Alum				4.6			2 ,,
Extract of indigo							r pint.
Gum-water (6 lbs. per ga	1.)						5 quarts.
No. 22. Drab Standard							
Purple liquor (see below,	No.	23.)					6 quarts.
Bark liquor, at 10° Tw.							ı quart.
Red liquor, at 20° Tw.							½ pint.
Extract of indigo							1 ,,
Different shades are made by the	addit	tion	of g	um-v	vate	г.	
			- 6				
No. 23. Purple Liquor.—	ntone	m n . f.	0	lina			= ==1
Lavender liquor (No. 12,							I gal.
Oxalic acid		• •				• •	3 ozs.
No. 24. Drab Standard, Silver	y.—						
_							3 gals.
Standard blue (No. 6)							2 ,,
Lavender liquor (No. 12,	stea	ms f	or ca	lico)		* *	I gal.
No. 25 Drab, Dark							
Gall liquor, at 12° Tw.							2 quarts.
Berry liquor, at 10° Tw.							r pint.
Cochineal liquor, at 6° To	W.						I gill.
Iron liquor, at 24° Tw.							I ,,
Gum-water							3 quarts.
No. 26. Drab, Dark							
Lavender liquor							3 quarts.
Blue standard, No. 6							2 11
Berry liquor, at 6° Tw.							3 pints.
							5 lbs.
							5
No. 27. Green—		2	T				1 .
Berry liquor or bark liquo						• •	4 gals.
	• •			• •	• •	• •	3 lbs.
Starch		* *		. 1		• •	6 ,,

Boil and add—							
Yellow prussiate, ground						4.2	6 lbs.
Tin crystals							ı lb.
							I ,,
Extract of indigo							23 pints.
No. 28. Pale Green							
Berry liquor, at 6° Tw.							3 quarts.
							13 lbs.
Alum							ol ozs.
Acetic acid							g pint.
Gum Senegal water (4 lbs							16 quarts.
Muriate of tin, at 120° To							8 ozs.
Extract of indigo							å pint.
· ·			٠.	٠.	• •	• •	4 pint.
No. 29. Green, Medium							
							8 quarts.
Yellow prussiate						٠.	3 lbs.
Alum							$I_{\frac{1}{2}}$,,
Gum-water (at 6 lbs. per	gal.)					7 quarts.
Water							ı quart.
Acetic acid							I ,,
Muriate of tin, at 120° T	W.						14 ozs. (weight.
Extract of indigo							I pint.
No. 30. Green, Dark							
							ı gal.
Red liquor, at 20° Tw.							5 pints.
Starch							1 lb. 13 ozs.
Boil and add—							5
Extract of indigo							ı lb. ı oz.
Alum							IO ozs.
							3 lbs. 2 ozs.
							I lb. 4 ozs.
Oxalic acid							5 ozs.
No. 31. Green, Dark							
Bark liquor, at 15° Tw.							2 gals.
Gum-substitute							1 lb.
Boil and add—		٠.	• •	• •		• •	1 40.
Alum							11 lbs.
Crystals of tin							4 OZS.
							3½ lbs.
Yellow prussiate							$3\frac{1}{2}$ 17
Oxalic acid (in 1 gill hot							32 17 4 OZS.
Extract of indigo		,					ı pint.
9				• •			- P
No. 32. Green, Dark.							,
Bark liquor, at 13° Tw.							0
Starch							ı∤ lbs.

Boil and add								
Alui Cool and add	n		• •	• •	• •	• •	• •	7} ozs.
Yell	ow prussiate							ı lb. 1½ ozs.
Tart	aric acid							83 ozs.
	lic acid							2 ,,
	act of indigo							6 ,,
Tin	pulp		• •	• •	• •	• •	• •	12 ozs. measure.
No. 33. G								
	k liquor, at 6° T							r gal.
Star	ch					• •	• •	14 lbs.
Boil and add								
Aluı	n							4 0ZS.
Cool and add								
	ow prussiate							g ozs.
	lic acid							3
	act of indigo			• •				10 ,,
Tin	pulp			٠.			• •	½ gill.
No. 34.	reen							
Bern	y liquor, at 13°	Tw						r gal.
Red	liquor, at 14° T	`w						I quart.
	m (in 🖁 gal. boil	-	,					½ lb.
	ow prussiate							₃ lb.
	lic acid			• •			٠.	1/4 "
	ract of indigo				• •	• •	• •	1/8 ,,
	pulp	• • • • •			• •			4 11
	n-water							
								finite extent both
in depth of s	hade and in ton	es borde	ering	more	on t	he b	olue o	or on the yellow.
No. 35. 1	ilac.—							
Lav	ender liquor (N	o. 12 ste	ams	on ca	alico)			2 gals.
Oxa	lic acid							6 ozs.
Ext	ract of indigo.							2 ,,
No. 36. 1	Lilac, Dark.							
	wood liquor, at	12° Tw.						4 gals.
Alu	m							3½ lbs.
Gur	n							12 ,,
No. 37.	Lilac, Dark							
	ender liquor (N	o. 12, st	eams	cali	co, st	rong	gest)	ı gal.
Pin	k standard (N	0. 35,		do.		d	o.)	Ι ,,
Gui	n-substitute							
No. 38.								
	ender liquor (a	s above)						I quart
	ry liquor, at 10°							-
	m Senegal wate							•

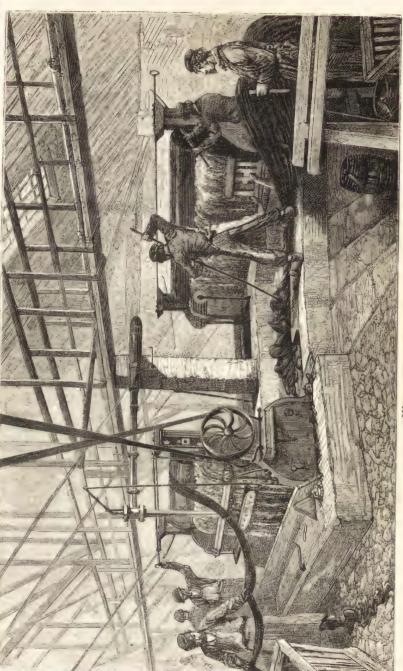
No. 39	Olive.—	
	Dark green (any of the above mentioned) 2 quarts	
	Lavender liquor (strongest) 1 quart.	
No. 40	o. Orange.—	
	Berry liquor, at 10° Tw 3 gals.	
	Gum Senegal	
	Red mordant (see No. 41) 3 pints	
	Tin crystals 12 ozs.	
Boil the	whole for fifteen minutes.	
No. 41	. Red Mordant.—	
	Water, hot	
	Alum 6 lbs.	
	Acetate of lead, white 3 ,,	
Stir till	all is dissolved; let settle, and decant the clear liquid for use.	
No. 42	orange, Red.—	
	Bark liquor, at 19° Tw 2 quarts	
	Starch	
	Water	
Boil, an	d add—	
	Cochineal liquor, at 8° Tw ‡ pint	
	Tin crystals	
The tor	e can be modified by increasing or diminishing the proporti	on
cochine	l liquor.	
No. 4:	3. Pink.—	
	Ammoniacal extract of cochineal, at 10° Tw 2 gals.	
	Best tartar	
	Alum	
	Gum 8 lbs.	
No. 4	4. Purple.—	
	Lavender liquor (strongest)	
	Binoxalate of potash 2 ozs.	
	Oxalic acid 2 ,,	
This co	lour may be modified by adding to it various proportions	of
mixture		
	Red liquor, at 18° Tw 3 quarts	
	Extract of indigo, neutral r quart.	
No. 4	5. Red, Pale.—	
	Ammoniacal cochineal liquor I gal.	
	Alum 4 ozs.	
	Tin crystals 4 "	
	Oxalic acid 4 "	
	Gum Senegal water (6 lbs. per gallon) I gal.	
No. 4	5. Red, Blotch.—	
	Cochineal liquor, at 6° Tw 12 gals.	
	Berry liquor, at 9° Tw 2 ,,	
	Starch 21 lbs.	
	Oxalic acid	
	Tin crystals $4\frac{1}{3}$ n	

NT a	D.J.4				,		
140*	47. Red, Amaranth.—						
	Ammoniacal cochineal paste			• •			rs lbs.
	Boiling water			• •	• •		4 gals.
	Alum			• •	• •		ı quart
	Gum				• •		18 lbs.
Dissolv	ve, and add—		• •	• •	• •	• •	10 105.
	Hydrochloric acid (pure) Bichloride of tin, at 100° Tw		• •				ı quart
No.	48. Scarlet.—						7
	Cochineal liquor, at 12° Tw.						2 gals.
	Starch				• •		4 lbs.
Boil, an	nd add—						
	Oxalic acid						4 ozs.
	Binoxalate of potash						4 ,,
	Pink salts	• •		2 6			8 ,,
	Tin crystals		* *	• •	* *	• •	8 ,,
No. 4	9. Scarlet						
	Standard (see below)						3 gals.
	Berry liquor, at 10° Tw						I quart
	Starch						43 lbs.
Boil, an	d add—						
	Binoxalate of potash						1 lb.
	Oxalic acid						1 ,,
	Pink salt						11 lbs.
	Tin, oxymuriate, at 120° Tw.					• •	I pint.
No. 50	o. Scarlet Standard						
	Cochineal, ground						2 lbs.
	Water						6 quarts
	Red liquor, at 20° Tw						I quart
	Nitric acid						4 ozs.
	Oxalic acid	• •					2 11
Boil for	twenty-five minutes, and strain	off t	the cl	ear	for	ise.	
No. 51	t. Yellow.—						
	Berry liquor, at 10° Tw						4 gals.
	Starch						51 lbs.
	British gum (pale)			• •			I lb.
	Tin crystals				• •	* *	ı₃ lbs.
No. 52	. Yellow (Lemon)						
	Berry liquor, at 41° to 5° Tw.						ı gal.
	Gum						3 lbs.
	Alum		• •		٠.		8 ozs.
	Oxalic acid	• •	• •	• •	• •		I ₂ ,,
	Perchloride of tin, at 100° Tw.		• •	• •		• •	8 ,,

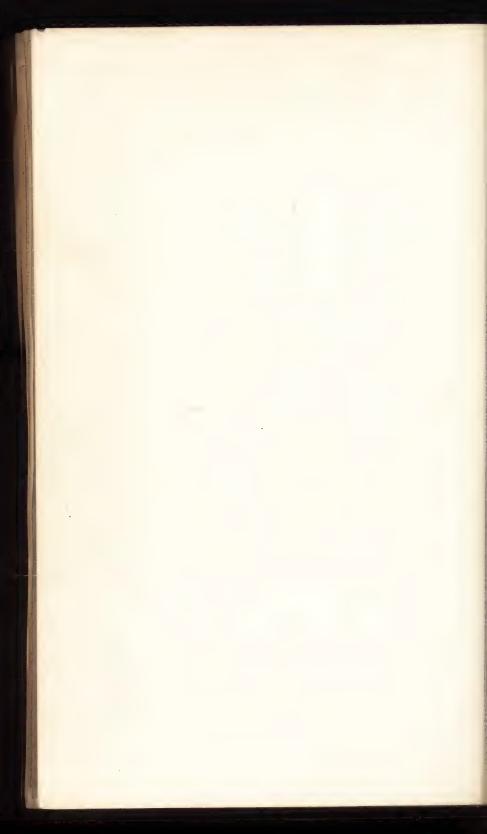
Woollen Goods.

Receipts for producing the usual colours on goods composed entirely of wool may be conveniently given here.

7 3				
No. 1. Black (Block)				
Calcined starch				to lbs.
				5½ quarts
9 7 7				142 ,,
				Il pints
FD 4.41				5 quarts
27.				3½ lbs.
771				2} quarts
T 11 . 0.073				-
				I 4 ,,
No. 2. Black (Blotch).				
				9 quarts
A 4 /		• •		9 ,,
				2; lbs.
Boil, and add before cooling—				
				ą 1b.
Sulphate of iron			٠.	12 11
Extract of indigo				3 ***
When cold add—				
Nitrate of iron, at 80° Tw				ra lbs.
No. 3. Black (for French Merinos)				
Logwood liquor, at 10° Tw.				61 quarts
Orchil liquor, at 10° Tw. (blue shade			• •	
Starch Starch	,			2 ;; 21 lbs.
Gall or myrobalan liquor, at 20° Two		• •		a pint
Boil, and add—				& buit
•				0.000
Copperas				2 ozs.
		• •	• •	2 ,,
		• •	• •	12 ,,
When cold add—				
Nitrate of iron, at 80° Tw	• • • •	• •	* *	15 ,,
No. 4. Black (for Objects).—				
Boiling water				τ gal.
Sapan liquor, at 22° Tw.				1/2 :-
Logwood liquor, at 48° Tw		٠.		I ,,
Then add by degrees—				
Water				½ gal.
In which has been dissolved—				- 0
Bichromate				a 1b.
Thicken with—				
Starch				31 lbs.
0 1 1 1				4 ,,
Add while hot—				1 //
Sal-ammoniac				Il lbs.
Verdigris				2計 ,,
1 41 41 11 11 11				~ g 11



WASHING-MACHINE FOR BLACKS.



When partially cool add—	
Oxalic acid	rļ 1bs.
Mix intimately with—	
Oil of turpentine	l pint
When quite cold add—	
	3 1 lbs.
Extract of indigo	34 "
No. 5. Black (both for Blotch and Objects)	
Logwood liquor, at 5° Tw	i quart
	4 OZS.
Boil, and add when cold—	
Nitrate of iron, at 80° Tw	4 OZS.
Nitrate of copper, at 80° Tw	I OZ.
Gall liquor, at 5° Tw	5 ozs.
No. 6. Black.	
Logwood liquor, at 5½° Tw	I quart
Gall liquor, at 8° Tw	I gill
Orchil liquor	5 ozs.
Starch	6 ,,
Boil, and add while warm—	
Extract of indigo	2 1 0ZS.
When cold add—	
Nitrate of iron	7½ OZS.
No. 7. Blue, Dark	
	2 0ZS.
Water	I gal.
Boil, and while still hot work in—	
	1½ lbs.
	4 ozs.
	6 ,,
Alum	Ο ,,
No. 8. Blue, Dark (another shade).—	
Extract of indigo	
	2 ,,
	12 ,,
	gals.
The depth of the shade can of course be easily modified by a	

The depth of the shade can of course be easily modified by an increase or decrease of the gum-water, and the blue can receive a bloomier tone, if required, by a slight increase of the cochineal.

No.	9.	Blue,	Royal
-----	----	-------	-------

Oxalic	acid	 	 	 	 	 ½ lb.
Alum		 	 	 	 ٠.	 6½ ozs.
Water		 	 	 	 	 a gal.
Gum		 	 	 	 	 3% lbs.

When cold add-								
Perchlor	ide of tin							4 0ZS.
Red prus	ssiate							20 ,,
Nitrate o	of iron, at 80°	Tw.						13 ,,
No. 10. Brown	n, Maroon.—							
Bark liqu	uor, at 18° Ty	V						I quart.
	al liquor, at 5							r ,,
								1 lb.
Oxalic a								1 ,,
Alum								3 ozs.
	de of tin, at 1							5 ,,
	of indigo							I 1/2 ,,
	0	* * * * * * * * * * * * * * * * * * * *						~ 2 11
No. 11. Brow	72.—							
Bark liq	uor, at 18° Ty	V						21 gals.
Orchil li	quor, at II°	Γw						I gal.
Cochine	al liquor, at 6	5° Tw						21 gals.
Starch								41 lbs.
Boil and add-								
Alum				. ,				13½ ozs.
Oxalic a	cid							81,,
Perchlor	ide of tin							21 ,,
Extract o	of indigo							41 ,,
	U							
No. 12. Brow								
	quor, at 18° T							I quart.
	quor, at 18° 7						0 0	I ,,
Starch						0 0	0	Ilb.
Boil and add-								
Alum								4 0ZS.
Tartaric	acid				0 0			2 ,,
Coppera	s							2: ,,
No. 13. Buff.	o-Publishin							
Bark liq	uor, at 4° Tw	7						r gal.
Orchil li	iquor, at 22°	Tw						1 .,
								I 1 lbs.
No. 14. Choca	olate, Dark	-						
Orchil li	iquor, at 16°	Tw. (blu-	e) .					1½ gals.
								12 ozs.
								2 ,,
Oxalic a								2 ,,
Stir till the mixt								
								16½ ozs.
	d starch							161,,,
And add-								
Extract	of indigo							6 ozs.
	J							

No. 15. Chocolate, Medium	
Orchil liquor, at 16° Tw	2 quarts.
Gum-water	2 ,,
Extract of indigo	I OZ.
No. x6. Chocolate, Reddish.	
Orchil liquor, at 16° Tw	ı gal.
Ammoniacal cochineal paste	71 ozs.
Alum	4 ,,
Oxalic acid	I OZ.
Sal-ammoniac	4 028.
	4 0000
Stir well till it ceases to froth, strain, and add-	- 11-
Starch	ı lb.
Extract of indigo	3 ozs.
No. 17. Green, Dark	
Bark liquor, at 17° Tw	11 gals.
Extract of indigo	3 lbs.
Sal-ammoniac	3 ozs.
Sulphate of alumina	r 1 lbs.
Dissolved in—	
Water	3 pints.
Tartaric acid	IO OZS.
Oxalic acid	7 ,,
Cool down and add—	
Perchloride of tin	IO OZS.
Yellow prussiate	4 17
Gum-substitute, according to the pattern.	
No. 18. Green, Dark	
	2 gals.
Extract of indigo	ri lbs.
Alum	ı lb.
	3 lbs.
Gum, powdered	3 105.
	8 ozs.
When cold add—	0 02/01
Oxalic acid	2 OZS.
Perchloride of tin, at 100° Tw	a lb.
	2
No. 19. Green, Lighter	
Fustic yellow, at 12° Tw	ı gal.
Extract of indigo	⅓ lb.
Alum	13 lbs.
Tartaric acid	б ozs.
Oxalic acid	3 11
Gum-water	2 gals.
Perchloride of tin, at 100° Tw	1/2 lb.
	4 .4

For the brightest greens, berry-liquor is generally employed as the yellow constituent. Small amounts of cochineal liquor are occasionally added to give more bloom and brightness to the blue constituent.

No. 20. Grey, Dark		
		2 gals.
White tartar		ı lb.
Alum		8 ozs.
Extract of indigo		8 ,,
Berry liquor, at 7° Tw		r quarts
Thickening according to the pattern. For lighter sha		
water, and increase the proportion of the acids.		9
NI DI. C		
No. 21. Pearly Grey.—		a 11.
0	• • • •	å lb.
		6 gals.
	* * * *	
		2 ,,
*		1½ ,, 8 gals.
		o gars.
Perchloride of tin, at 100° Tw		I g IDS.
No. 22. Grey, Dark.—		
Logwood liquor, at 6° Tw		r gal.
Nitrate of iron, at 80° Tw		10 ozs.
Gum-water		I gal.
No. 23. Lilac.—		
Ammoniacal cochineal liquor		∦ gal.
Acetic acid (weak)		ı quart.
Alum		TO OZS.
Oxalic acid		8 ,,
		2 lbs.
		6 ozs.
		2 gals.
No. 24. Orange.—		0
		2 gals.
		z gals.
		$6\frac{1}{4}$ lbs.
0 11 11		10 OZS.
		1 lb. 5 ozs.
		1 10. 5 025.
No. 25.—Pink.—		
Ammoniacal cochineal paste		ı lb.
1		Ι ,,
		2 gals.
Boil down to 11 gallons, and add—		
		6 ozs.
		12 ,,
Gum-water		2 gals.
No. 26. Yellow.—		
Berry liquor, at 11° Tw		ı gal.
		I4 ozs.
Gum		5 lbs.

No. 27. Yellow.—	
Bark liquor, at 18° Tw	gal.
	lb.
Alum 60	ozs.
	79
Oxalic acid 2	9.9
Gum 3	lbs.
Perchloride of tin, at 108° Tw 6	OZ.
No. 28. Orange-Yellow.—	
	gals.
	lbs.
Boil, and mix with—	2001
·	l lbs.
	lb.
	ozs.
(See p. 218).	025.
No. 29. Black on Woollen Yarn.—	
Extract of logwood (solid) 6	
Boiling water	pints.
Dissolve, let cool and settle, and add the clear liquid to—	
Iron liquor, at 7° Tw	
Nitrate of iron, at 88° Tw	
Gum tragacanth 1	11
The amount of gum is subject to modification as the case may r	
pieces, when printed, are exposed to the air for six hours, steam	
pieces, when printed, are exposed to the air for six hours, steam five minutes, rinsed, and dried.	
pieces, when printed, are exposed to the air for six hours, steam five minutes, rinsed, and dried. No. 30. Brown on Woollen Yarn.—	
pieces, when printed, are exposed to the air for six hours, steam five minutes, rinsed, and dried. No. 30. Brown on Woollen Yarn.— Extract of peachwood (solid)	ned for forty-
pieces, when printed, are exposed to the air for six hours, steam five minutes, rinsed, and dried. No. 30. Brown on Woollen Yarn.— Extract of peachwood (solid)	lbs.
pieces, when printed, are exposed to the air for six hours, steam five minutes, rinsed, and dried. No. 30. Brown on Woollen Yarn.— Extract of peachwood (solid)	lbs.
pieces, when printed, are exposed to the air for six hours, steam five minutes, rinsed, and dried. No. 30. Brown on Woollen Yarn.— Extract of peachwood (solid)	lbs. lb. ½ pints.
pieces, when printed, are exposed to the air for six hours, steam five minutes, rinsed, and dried. No. 30. Brown on Woollen Yarn.— Extract of peachwood (solid)	lbs. lb. ½ pints.
pieces, when printed, are exposed to the air for six hours, steam five minutes, rinsed, and dried. No. 30. Brown on Woollen Yarn.— Extract of peachwood (solid)	lbs. lb. pints.
pieces, when printed, are exposed to the air for six hours, steam five minutes, rinsed, and dried. No. 30. Brown on Woollen Yarn.— Extract of peachwood (solid)	lbs. lb. pints.
pieces, when printed, are exposed to the air for six hours, steam five minutes, rinsed, and dried. No. 30. Brown on Woollen Yarn.— Extract of peachwood (solid)	lbs. lb. pints.
pieces, when printed, are exposed to the air for six hours, steam five minutes, rinsed, and dried. No. 30. Brown on Woollen Yarn.— Extract of peachwood (solid)	lbs. lb. lb. lb. lb. lb. lb. lb. lb. lb. lb
pieces, when printed, are exposed to the air for six hours, steam five minutes, rinsed, and dried. No. 30. Brown on Woollen Yarn.— Extract of peachwood (solid)	lbs. lb. lb pints. lb. ly pints. location in the location in t
pieces, when printed, are exposed to the air for six hours, steam five minutes, rinsed, and dried. No. 30. Brown on Woollen Yarn.— Extract of peachwood (solid)	lbs. lb. lb pints. lb. ly pints. location in the location in t
pieces, when printed, are exposed to the air for six hours, steam five minutes, rinsed, and dried. No. 30. Brown on Woollen Yarn.— Extract of peachwood (solid)	lbs. lb. lb. lpints. lb. lyints. lb. lyints. lpints. lyints. lyints. lyints. lyints. lyints. lyints. lyints. lyints.
pieces, when printed, are exposed to the air for six hours, steam five minutes, rinsed, and dried. No. 30. Brown on Woollen Yarn.— Extract of peachwood (solid)	lbs. lb. lb. lpints. lb. lpints.
pieces, when printed, are exposed to the air for six hours, steam five minutes, rinsed, and dried. No. 30. Brown on Woollen Yarn.— Extract of peachwood (solid)	lbs. lb. lpints. lb. lpints. lb. lpints. lib. lpints.
pieces, when printed, are exposed to the air for six hours, steam five minutes, rinsed, and dried. No. 30. Brown on Woollen Yarn.— Extract of peachwood (solid)	lbs. lb. lpints. lb. lpints. lb. lpints. lib. lpints.
pieces, when printed, are exposed to the air for six hours, steam five minutes, rinsed, and dried. No. 30. Brown on Woollen Yarn.— Extract of peachwood (solid)	lbs. lb. lpints. lb. lpints. lb. lpints. lib. lpints.
pieces, when printed, are exposed to the air for six hours, steam five minutes, rinsed, and dried. No. 30. Brown on Woollen Yarn.— Extract of peachwood (solid)	lbs. lb. lpints. lb. lpints. lb. lpints. lib. lpints.
pieces, when printed, are exposed to the air for six hours, steam five minutes, rinsed, and dried. No. 30. Brown on Woollen Yarn.— Extract of peachwood (solid)	lbs. lb. lb. lpints. lb. lpints. lb. lpints.
pieces, when printed, are exposed to the air for six hours, steam five minutes, rinsed, and dried. No. 30. Brown on Woollen Yarn.— Extract of peachwood (solid)	lbs. lb. lb. lpints. lb. lpints. lb. lpints.

Boil and strain; exhaust the residue with further portions of water, mix the extracts, concentrate to 10½ pints; cool and let settle. In the clear liquor dissolve—

	Oxalic acid		 	 	 	 	5 ozs.
	Tin crystals		 	 	 	 	21 ,,
Thicken	with-						
	Wheat stare	ch	 	 	 	 	½ 1b.
	White glue		 	 	 	 	1 77
	eam at 100°						

No. 33. Scarlet for Woollen Yarn .-

The mixture is the same as for ponceau, but from \(\frac{1}{4}\) to \(\frac{1}{2}\) oz. of extract of fustic, previously dissolved in water, is added.

Silks.

There is in many cases a difficulty in preserving the whites—grounds or figures—clean, as the silk has in itself a considerable attraction for colours. Before the printing the goods are boiled for two hours with soap of a fine quality, in the proportion of 1 lb. of soap to 4 lbs. of material. They are then well rinsed in pure water, and dried. Every shade of colour can be produced on silk by the steaming process, with the advantage that the grounds remain unsullied. The goods are first prepared with tin, being steeped for four hours in sulpho-muriate of tin, at 2° Tw. After this process the silk is washed in clean water, and dried.

No. 1. Sulpho-Muriate of Tin, for Silks	D	issol	ve i	n wa	iter—
Tin crystals					ı lb.
And add—					
Sulphuric acid, at 170° Tw					ı lb.
And reduce with water to 2° Tw.					
No. 2. Blacks.—					
Logwood liquor, at 8° Tw					2 gals.
Iron liquor, at 10° Tw					I quart.
Flour					I lb.
British gum, light					I ,,
Boil, and add—					
Yellow prussiate					6 ozs.
When cold add—					
Sulphate of copper					2 OZS.
Muriate of iron, at 80° Tw					I pint.
Nitrate of iron, at 80° Tw					ı gill.
No. 3. Black, for Grounds					
Logwood liquor, at 8° Tw					2 gals.
Acetate of copper (liquid), at 40° T					r pint.
Red liquor, at 18° Tw					32 ozs.
Starch					21 lbs.
Boil, and after cooling add-					-
Nitrate of iron, at 80° Tw					14 028.

	Si	ILKS.					63.
No. 4	. Black (Cylinder or Block).						
	Logwood liquor, at 14° Tw.						2 gals.
	Starch						ri lbs.
	British gum	* *					31 "
Boil, co	ol, and add—						
	Nitrate of copper (crystals)						I lbs.
	Nitrate of iron						ı lb.
No. 5	. Black.—						
	Logwood liquor, at 6° Tw						2 gals.
	Galls, in fine powder						7 ozs.
Boil do	wn to I gallon, to which add-						•
	Starch						I lb. 10 ozs.
Boil, an	d when cold add-						
	Alum						2 OZS.
	Sulphate of copper						63,,,
	Copperas						2 ,,
	Nitrate of iron, at 80° Tw				• •	• •	4½ ,,
	Palm or cocoa-nut oil			• •		• •	5½ "
No. 6	. Blue.—						
	Logwood liquor, at 15° Tw.						r gal.
	Red liquor, at 15° Tw.						Ι ,,
	Ground gum						10 lbs.
When a	ll is dissolved add—						
	Tartaric acid						IO OZS.
	Nitrate of copper, at 80° Tv				• •		10 ,,
	Extract of refined indigo			• •	• •	• •	ı gal.
No. 7	. Blue (Extract of Indigo)	_					
	Extract of indigo (finest)						3 lbs.
							ı gal.
	Alum						8 ozs.
	Tartaric acid						Ilb.
	Gum						6 lbs.
No. 8	. Royal Blue.—						
	Yellow prussiate			, ,			3 lbs.
	Hot water						r gal.
When d	issolved add—						- 6
***********	Tartaric acid						ıı 1bs.
When co	old thicken with—						
	Gum, ground						7 lbs.
Add—							•
	Perchloride of tin, at 80° Tv					e • •	2½ lbs.
These	mixtures are to a great exter	nt sup	ersec	ded l	y th	e ani	line blues, which

These mixtures are to a great extent superseded by the aniline blues, which produce the finest effects upon silk.

No.	8 a.	Blue
-----	------	------

 	 					ı gal.
 	 					Ilb.
	 at 170° Tw.	at 170° Tw				

No. 9. Brown .-

ļ٠	Drown.				
	Berry liquor, at 6° Tw		 	 	I pint.
	Logwood liquor, at 3° Tw.		 	 	16 ozs. (measure).
	Sapan liquor, at 3 Tw	4 +	 	 	3 quarts.
	Starch		 ٠.	 	ı lb.
	Alum		 	 	1
	Nitrate of copper, at 80° Tw.		 	 	1 22

Perchloride of tin, at 80° Tw...

No. 10. Brown .-

Berry liquor, at 101° Tw	 	 	 2 gals.
Peachwood liquor, at 7 Tw.	 	 	 I 1/2 ,,
Logwood liquor, at 7½° Tw.	 	 	 3 quarts
Alum	 	 	 2 ½ lbs.
Sulphate of copper	 	 	 14 ,,
Gum, for thickening, about	 	 	 8 ,,

Here, also, fine effects may be produced with the coal-tar browns. (See also p. 209.)

No. 11. Chocolate. -

Sapan liquor, a	t I2°	Tw.	 	 	 	2 gals.
Logwood liquo						
Bark liquor, at	16° 7	. W.	 	 	 	ı quart.
Alum						
Sal-ammoniac			 	 	 	I ½ ,,
Gum Senegal			 	 		T.4

No. 12. Chocolate (Heavy) .-

Sapan liquor, at 20° Tw		 		 	2 gals.
Logwood liquor, at 20° Tv	V.	 		 	2 quarts.
Alum		 		 	20 OZS.
Sal-ammoniac		 	٠.	 	₁ lb.
Verdigris		 		 	ı lb.
Gum		 		 	to lbs.

No. 13. Chocolate .-

Sapan liquor, at 5° Tw	 	 	 2 gals.
Berry liquor, at 10° Tw			
Logwood liquor, at 5° Tw.	 	 	 z gals.
Starch	 	 	 5 lbs.
Gum-substitute	 	 	8

												~33
Boil, ar	nd add whi	ile still v	varn	1-								
A m d worls	Alum nen cold—					• •	* *		• •		2½ lbs.	
And Wi	Sulphate	of copp	er								Ilbs.	
No. 1	t4. Choco	late										
	Sapan lie										2 gals.	
	Berry liq	uor, at	1710	Tw.							21/2 ,,	
	Logwood	l liquor,	at I	9° T	V.						I 8 ,,	
	Gum, gre	ound									30½ lbs.	
	Alum										41 .,	
	Sal-amm	oniac									r 1b.	
	Verdigris										13 lbs.	
No. 1	15. Green											
	Berry liq	uor, at	[420	Tw.							ı gal.	
	Gum										2 lbs.	
After di	issolving a	.dd—										
	Extract o	of indigo									7½ ozs.	
	Tartaric	acid sol	ution	ı, at	38° ′	Γ_{W} .					4 11	
	Permuria	ite of tir	n, at	80° ′	Γ w.						2 ,,	
No. T	6. Green											
21012	Yellow c		ee be	low.	No.	26.)					I gal.	
		,				,					ı gill.	
	Double r	nuriate (of tir	ı, at	120°	Tw.					2½ ozs.(me	easure.)
The	most book		01 111	2, 000	120						220001(1116	
		ITITIL OT	eens	are	now	r. ho	wev	er. c	btai	ned	with the	antline
											with the	
greens	(aldehyd,	iodine, c	or me	thyl), wi	th a	ddit	ions	of p	icric	acid if y	ellower
greens tones ar	(aldehyd, re wanted	iodine, c (see p. 2	or me 206).	thyl A), wi good	th a	ddit en n	ions nay a	of p Iso l	icric	acid if y	ellower adding
greens tones ar to the b	(aldehyd, re wanted lue colour	iodine, c (see p. 2 No. 8a	or me 206). , picr	thyl A), wi good	th a	ddit en n	ions nay a	of p Iso l	icric	acid if y	ellower adding
greens tones ar to the b	(aldehyd, re wanted blue colour Grey,	iodine, c (see p. 2 No. 8a,	or me 206). , picr	thyl A), wir good cid, r	th a gree nore	ddit en n or l	ions nay a ess,	of p Iso I acco	icric be o rdin	acid if y btained by g to shade	ellower adding
greens tones ar to the b	(aldehyd, re wanted blue colour Grey, Logwood	iodine, c (see p. 2 No. 8a, Dark.— I liquor,	or me 206). picr at 6°	thyl A ic ac), wi good cid, r	gree nore	ddit en m or l	ions nay a ess,	of p Iso I acco	icricose of rdin	e acid if y btained by g to shade I gal.	ellower adding
greens tones ar to the b	(aldehyd, re wanted blue colour 17. Grey, Logwood Nitrate o	iodine, c (see p. 2 No. 8 a Dark.— I liquor, of iron, a	or me 206). picr at 6°	A ric ac), wi good cid, r	th a gree	dditen m	ions nay a ess,	of p Iso I acco	icricose of rdin	acid if y btained by g to shade. I gal. l lb.	ellower adding
greens tones ar to the b	(aldehyd, re wanted blue colour 17. Grey, Logwood Nitrate of Tartaric	(see p. 2 No. 8 a. Dark.— I liquor, of iron, 2	or me 206). , picr at 6°	A ric ac), wi good cid, r	th a gree	ddit en m or l	ions hay a ess,	of p Iso I acco	icricope of rdin	e acid if y btained by g to shade I gal. 1 lb. 1 oz.	ellower adding
greens tones ar to the b	(aldehyd, re wanted blue colour 17. Grey, Logwood Nitrate o	(see p. 2 No. 8 a. Dark.— I liquor, of iron, 2	or me 206). , picr at 6°	A ric ac), wi good cid, r	th a gree	ddit en m or l	ions nay a ess,	of p Iso I acco	icricope of rdin	e acid if y btained by g to shade. I gal. d lb. d oz.	ellower adding
greens tones an to the b	(aldehyd, re wanted blue colour 17. Grey, Logwood Nitrate of Tartaric	(see p. 2 No. 8a, Dark.— I liquor, of iron, a	or me 206). , picr at 6°	A ric ac), wi good cid, r	th a gree	ddit en m or l	ions hay a ess,	of p Iso I acco	icricope of rdin	e acid if y btained by g to shade I gal. 1 lb. 1 oz.	ellower adding
greens tones at to the b No. 1	(aldehyd, re wanted blue colour r. Grey, Logwood Nitrate of Tartaric Gum	(see p. 2 No. 8a. Dark.— I liquor, of iron, a acid	or me 206). , picr - at 6° at 80°	A ric ac), wii good cid, r	th a greenore	ddit en m or l	ions hay a ess,	of p Iso I acco	icricope of rdin	e acid if y btained by g to shade I gal. 1 lb. 1 oz.	ellower adding
greens tones at to the b No. 1	(aldehyd, re wanted olue colour (7. Grey, Logwood Nitrate of Tartaric Gum (7a. Oran solution of the colour (7a. Oran solution of the	odine, of (see p. 2 No. 8 a. Dark.— I liquor, of iron, a acid	or me 206). picr at 6° at 80°	A ric ac Tw Tw Tw), wi good cid, r	th a greenore	dditten mor l	ions nay a ess,	of p Iso I acco	ierico oe o rdin	e acid if y btained by g to shade I gal. 1 lb. 1 oz.	ellower adding
greens tones at to the b No. 1	(aldehyd, re wanted olue colour (7. Grey, Logwood Nitrate of Tartaric Gum (7a. Oran solution of Annatto	iodine, co (see p. 2 No. 8 a. No. 8 a. Dark.— I liquor, of iron, a acid	or me 206). picr at 6° at 80°	Two Two), wi good cid, r	th a greenore	dditten mor l	ions hay a ess,	of p Iso I acco	rdin	e acid if y btained by g to shade I gal. I lb. Output Output I lb. I oz. I lbs.	ellower adding
greens tones at to the b No. 1	(aldehyd, re wanted blue colour (7. Grey, Logwood Nitrate of Tartaric Gum (7a. Oran solution of Annatto Pearl-ash	iodine, co (see p. 2 No. 8 a. No. 8 a. Dark.— I liquor, of iron, a acid	or me 206). picr at 6° at 80°	ethyl A ic ac Tw Tw mix), wirgood cid, r	th a gree nore	dditten mor l	ions nay a ess,	of p Iso I acco	ordin	e acid if y btained by g to shade I gal. I lb. Output Output I lb. I oz. I lbs.	ellower adding
greens tones at to the b No. 1 No. 1 Make a	(aldehyd, re wanted blue colour (7. Grey, Logwood Nitrate of Tartaric Gum (7a. Oran solution of Annatto Pearl-ash Water	iodine, co (see p. 2 No. 8 a. No. 8 a. Dark.— 1 liquor, of iron, a acid	or me 206). picr at 6° at 80°	A ric ac Tw Tw mix), wirgood cid, r	th a green nore	ddit en m or l	ions nay a ess,	of p Iso I acco	control of the contro	r acid if y btained by g to shade. I gal. 4 lb. 2 oz. 4 lbs. 4 lbs. 6 gals.	ellower adding
greens tones at to the b No. 1 No. 1 Make a	(aldehyd, re wanted blue colour (7. Grey, Logwood Nitrate of Tartaric Gum (7a. Oran solution of Annatto Pearl-ash	iodine, co (see p. 2 No. 8 a. Dark.— I liquor, of iron, a acid	at 6° to by	A A Two mix), wi good cid, r	th a greenore	ddit ddit or l	ions hay a ess,	of place of	cdd-	r acid if y btained by g to shade. I gal. 4 lb. 2 oz. 4 lbs. 4 lbs. 6 gals.	ellower adding
greens tones at to the b No. 1 No. 1 Make a	(aldehyd, re wanted blue colour (7. Grey, Logwood Nitrate of Tartaric Gum (7a. Oras solution of Annatto Pearl-ash Water is down to Gum-wa (7b. Cora	iodine, co (see p. 2 No. 8 a; No. 8 a; Dark.— 1 liquor, of iron, a acid	or meerool., picrometrool., picromet	A Two mix), wirggood good, r the gal.)	th a gree more	ddit or l	ions anay a ess,	of p	oce of control of the	r acid if y btained by g to shade I gal. I lb. Output L lbs. I lbs. I gals. I gal.	ellower adding
greens tones at to the b No. 1 No. 1 Make a Boil thi	(aldehyd, re wanted blue colour (7. Grey, Logwood Nitrate of Tartaric Gum (7a. Oran solution of Pearl-ash Water (1s down to Gum-wa (7b. Coralline Coralline (1s))	iodine, co (see p. 2 No. 8 a. No. 8 a. 1 liquor, of iron, a acid	or me (206). , picr at 6 of at 80 of at	A Two Two mix	the gal.)	th a gree green nore	ddit or l	ions anay a ess,	of p	icric	r gal. d lbs. d lbs. d lbs. g gal. d lbs.	ellower adding
No. I No. I No. I Soda at	(aldehyd, re wanted blue colour (7. Grey, Logwood Nitrate of Tartaric Gum (7a. Oran solution of Annatto Pearl-ash Water is down to Gum-wa' (7b. Coralline to 'B., e	iodine, co (see p. 2 No. 8 a. No. 8 a. liquor, of iron, a acid	or me (206). , picro at 6 of the to by Run lbs. ange-	Two mix	the gal.)	th a greed g	ddit or l	ions hay a ess,	of p p lso 1	icricione o rdin	r gal. d lbs. d lbs. g gal. d lbs. d lbs. z gal. d lbs. d lbs. d lbs. p gal. d lbs. l pal. d lbs. l pal.	ellower adding
No. I No. I No. I Soda at	(aldehyd, re wanted blue colour (7. Grey, Logwood Nitrate of Tartaric Gum (7a. Oran solution of Annatto Pearl-ash Water (8 down to Gum-war Coralline to '8 B., ee to 'B.; hez	iodine, co (see p. 2 No. 8 a. No. 8 a. 1 liquor, of iron, a acid	or meeof). , picr at 6' at 80' Run lbs. ange. o disand	Two	the ggal.)	cclean	ddit or l	ions ay a ess, I ga h wa thus	of poor of poo	add	r gal. g lbs.	ellower adding
No. I No. I No. I Soda at	(aldehyd, re wanted blue colour (7. Grey, Logwood Nitrate of Tartaric Gum (7a. Oran solution of Annatto Pearl-ash Water (7b. Coral line to 'B., e (50' B.; hea Magnesis	iodine, co (see p. 2 No. 8 a.	or meeof). , picr at 6' at 80' Run lbs. ange o disand	Two	the ggal.)	th a gree	ddit or l	ions anay a sess,	of plass of	add	r gal. g lbs.	ellower adding
No. I No. I No. I Soda at	(aldehyd, re wanted olue colour (7. Grey, Logwood Nitrate of Tartaric Gum (7. Gra. Oran solution of Annatto Pearl-ash Water is down to Gum-wa (7. Coralline to '8., e o '8.; hea Magnesic Oxalic ac	iodine, co (see p. 2 No. 8 a.	or meeoob., picro at 6' at 80' Run lbs. ange. o dis and	A Two Two mix	ing— the gal.) e; der. T	th a green nore	ddit	ions hay a ess,	of plass lacco	add	acid if y btained by g to shade. I gal. I lb. Output I bs. I bs. I gal. I lbs. I gal. I lbs. I gal. I lbs. I gal. I gal.	ellower adding
No. I No. I No. I Soda at	(aldehyd, re wanted olue colour (7. Grey, Logwood Nitrate of Tartaric Gum (7. Oran solution of Annatto Pearl-ash Water is down to Gum-wa' (7b. Coral line to 'B., e o' B.; hea Magnesia Oxalic au Gum, in	iodine, co (see p. 2 No. 8 a.	or me eoo(). , picro at 6' at 80' Run lbs. ange- o dis and	A Two Two Min off per second filte	on the gal.)	th a green nore	dditten m or l	ions hay a ess,	of plso 1 lso 1 ls	add-	acid if y btained by g to shade. I gal. I lb. Output I bs. I bs. I gal. I lbs. I gal. I lbs. I gal. I lbs. I gal. I gal.	ellower adding .

Mix well, heat, and strain; print and expose for ten hours before steaming for thirty to forty minutes.

inirty to forty minutes.			
No. 18. Pink.—			
Sapan liquor, at 6½° Tw			I gal.
Gum, in powder			3 lbs.
Perchloride of tin, at 120° Tw			4 ozs.
No. 19. Pink.—			
Ammoniacal cochineal liquor, at 6	° Tw		2 quarts
Binoxalate of potash			3 ozs.
Perchloride of tin, at 120° Tw.			I ½ ,,
			2 quarts
No. 20. Pink.—			•
Ammonical cochineal liquor, at 6°	Tw		2 quarts
Alum			2 OZS.
Oxalic acid			$\frac{1}{4}$ OZ.
Gum-water, at 6 lbs. per gallon			2 quarts
Saffranin yields the most beautiful pinks ar			silk (see p. 207).
No. 21. Purple.	0	•	
Logwood liquor, at 3° Tw			r gal.
Sapan liquor, at 3° Tw			I ,,
Alum			4 lbs.
			3 "
Digest at a gentle heat for several hours			
alum is completely dissolved and the sedin			
liquor. Of this take 2 quarts.			
Gum-water, at 6 lbs. per gallon			2 quarts
			3 ozs.
Nitrate of alumina			I OZ.
Oxalic acid			
For purple and violet shades the aniline of	colours, s	uch as H	ofmann's violets,
have a decided advantage (see p. 195.)			
No. 22. Red.—			
Cochineal liquor, at 4° Tw			3 gals.
Bark liquor, at 12° Tw			I! pints
Starch			3 lbs.
Boil, and when cool add—			
Oxalic acid			I 1b.
Tin crystals			ı ,,
No. 23. Red (Crimson Shade)			
Ammoniacal cochineal paste			2 lbs.
Water			I gal.
Boil and strain; then add-			
Gum (ground)			2 lbs.
Alum			3 028.
Acetate of lead			2 ,,
Tartaric acid			I OZ.
Perchloride of tin			4 ozs.

No. 24. Scarlet					
Cochineal liquor (strong)					3 gals.
Starch	,				2 lbs.
Boil and add—					
Berry liquor, at 15°					5 OZS.
Fustic liquor, at 15°					
Binoxalate of potash					14 ,,
Tin crystals					21,
Perchloride of tin, at 100° Tw.					-
·					2 71
No. 25. Yellow.—					
Bark liquor, at 16° Tw					3 gals.
Alum					½ lb.
Tin crystals U					3 ozs.
Oxalic acid					3 ,,
Gum Senegal		• •		• •	g lbs.
No. 26. Yellow.—					
Berry liquor, at 12° Tw					I gal.
Alum					₹ lb.
Tin crystals					8½ ozs.
Gum					3 lbs.
No. 27. Yellow					
Water					ı gal.
Turmeric					1 gar.
Berries					I 1 ,,
	• •	• •			1 2 1,
Boil down to 2 quarts, and add—					
Tin crystals					
Alum					½ lb.
Gum, according to shade, about		* *		• •	I lb.
Ninth Style.—Spirit Colours	n (A	221	ooti	on C	(1010000)
Athth Style.—Spirit Colour.	20 (A)	ווחח	vall	UII C	OLUUIS.)

Ninth Style.—Spirit Colours. (Application Colours.)

Spirit colours are very brilliant, but not permanent. They derive their name from the large proportion of "spirits," a technical name for acid solutions of tin, which enters into their composition. Steaming is impracticable owing to the great acidity of the mixtures; the printed pieces consequently are dried at a gentle heat, exposed in the ageing room for a few hours, rinsed, washed in cold water, and finally dried.

No. 1	. Black									
	Logwoo	od liq	uor,	at 89	Tw		 	 	 I	gal.
	Water						 	 	 I	2.1
	Coppera	as					 	 	 10	ozs.
	Starch						 	 	 3	lbs.
Boil and	l add—									
	Nitrate	of in	on, a	at 80	Tv	7	 	 	 1	gill.
No. 2.	Blue	_								
	Water						 	 	 I	gal.
	Starch						 	 	 I	lbs.

Boil and let cool down to 108° F., and add-			
Tin pulp			1 quart
Perchloride of tin, at 120° Tw			I5 ozs.
No. 3. Blue.—			
Water			ı gal.
Yellow prussiate			ı lb.
Alum			6 ozs.
Starch			Il lbs.
Boil, and after cooling down to 110° F., add			14
Nitrate of iron, at 80° Tw			15 ozs.
Perchloride of tin, at 20° Tw			15 ,,
referred of thi, at 20 1 w			13 ,,
No. 4. Blue (Block).—			
Water			I gal.
Yellow prussiate			ı lb.
Starch			11 lbs.
Boil briskly for a few minutes, and when co			
Nitrate of iron, at 80° Tw			Il gills
Perchloride of tin, at 100° Tw.			3 ,,
No. 7 Puosus			
No. 5. Brown.—			w ~ ~ 1
			I gal.
0 (0)			2 lbs.
Boil, and add—			11
<u> </u>		• • • •	r lb.
Spirit pink (No. 10)	• • • • •	• • • •	2 quarts
Spirit purple (No. 13)			2 ,,
No. 6. Chocolate.			
Spirit pink (No. 10)			23 gals.
Spirit blue (No. 3)			I gal.
			0
No. 7. Chocolate.—			
- 1 1 /			3 quarts
Logwood liquor, at 10° Tw			2 ,,
Bark liquor, at 13° Tw			I quart
Starch		* * * * *	2 lbs.
Boil, and let cool down to 110°, and add—			
Perchloride of tin, at 100° Tw	* * * * *		I pint
Nitrate of copper, at 80° Tw			$\frac{1}{2}$,,
Oil			Ι ,,
No. 8. Green			
Spirit blue (No. 3)			ı gal.
Spirit yellow (No. 15)			Ι ,,
			,,
No. 8a. Orange.			
Berry liquor, at 8° Tw			1½ gals.
British gum (light)	* * * * *	• • • •	12 lbs.
Boil, and add—			
Tin crystals			
Spirit pink (No. 10)			4 gals.

No. q. Pink.—					
Sapan liquor, at 14° Tw					I gal.
Sal-ammoniac					lb.
Gum-water, at 6 lbs. per gal					I gal.
Perchloride of tin, at 120° Tw					r pint
No. 10. Pink.—					
Sapan liquor, at 8° Tw					r gal.
Water					I ,,
Common salt					2 lbs.
Starch					I ½ ,,
Boil, and when cool add-					
Perchloride of tin, at 120° Tw					I pint
Nitrate of copper, at 80 Tw					3 ozs. (measure).
No. II. Pink.—					,
Peachwood liquor, at 8° Tw					7 mal
Starch	• •	• •		• •	· · ·
	• •	• •	• •		1 7 105.
Boil well together and add—					
Nitrate of copper, at 100° Tw	• •	• •	• •		½ gill
When cooled down to 100° F. add —					
Perchloride of tin, at 120° Tw					3 gills
Pink salt					**
Oil	• •		• •		I gill
No. 12. Pink.—					
Sapan liquor, at 8° Tw					I gal.
Starch					1½ lbs.
Boil, and when cooled down to 100° F., add	1—				
Perchloride of tin, at 120° Tw					3 gills
Acetate of copper					½ gill
No. 12a. Pinks for Blocking Madder W	ork.				
Sapan liquor, at 10° Tw					4½ gals.
Pink salt					9 lbs.
Sal-ammoniae					3 ,,
Sulphate of copper					2 ,,
Oxalic acid					5¼ ozs.
Water					I pint
Gum Senegal water (6 lbs. per gal	,				4½ gals.
Perchloride of tin, at 120° Tw		• •			1 guarts
No. 13. Purple.—					
Logwood liquor, at 8° Tw					ı gal.
Water					Ι ,,
Copperas					IO ozs.
Starch					2 lbs.
Boil, and add—					
					r pint
Perchloride of tin, at 120° Tw					1 ,,

N Dod	
No. 14. Red.— Sapan liquor, at 4° Tw 3 gals.	
Sal-ammoniac	
Verdigris	
Starch	
Boil, and when cool add—	
Pink salt 5 lbs.	
Oxalic acid	
No. 15. Yellow	
Berry liquor, at 10° Tw 1 gal.	
Alum 8 ozs.	
Starch Ilb.	
Boil and add—	
Double muriate of tin, at 120° Tw 1 pint	
Tenth Style.—Manganese Bronzes.	
This style, formerly in great demand, is now almost obsolete. The goo	ods
are padded in solutions of sulphate or chloride of manganese of vary	
strength according to the shade required. For medium shades the solut	ion
is about 80° Tw. After padding the goods are dried and padded once in so	da-
lye, at 24° Tw., and afterwards in a weaker lye, at 12° Tw. They are the	hen
rinsed in water, and afterwards in bleaching lime, at 2° Tw. This operat	ion
is continued till the pieces are perfectly brown all over. They are n	ext
washed in water and dried. The colours printed on this brown discharge	
and are fixed in its place, thus producing blue, green, pink, yellow, &	хс.,
designs on a brown ground.	
No. I. Blue.—	
Water 6 gals.	
Yellow prussiate 33 lbs.	
Starch	
British gum, light 6 lbs.	
Boil and add— Tartaric acid	
Oxalic acid	
Nitrate of iron	
Of this mixture 5 quarts are added to 3 quarts of double muriate of tin	ı. at
120° Tw.	,
No. 2. Yellow (to be followed up with Chrome).—	
Water I gal.	
Nitrate of lead 5 lbs.	
British gum, light 4 ,,	
Boil, and add—	
Tartaric acid 4 lbs.	
Of this mixture 3 quarts are added to 1 quart double muriate of tin, at 120°	Tw.
No. 3. Green.—	
No. I (without the tin) 2 quarts	
No. 2 (,, ,,)	
Double muriate, at 120° Tw	

No. 4. Pink.—	
Brazil-wood liquor, at 12° Tw	r gal.
Sulphate of copper	2 OZS.
Sal-ammoniac	2 ,,
Starch ,	2 lbs.
Boil, and add—	
Perchloride of tin, at 120° Tw	8 ozs. measure.
Mix 2 quarts of this with I of double muriate, at 120° Tw.	
No. 5. White.—	
Water	2 gals.
British gum, light	8 lbs.
Boil, and add—	
Tartaric acid	8 lbs.
Double muriate of tin, at 120° Tw	I gal.
No. 6. Black.—	
Logwood liquor, at 8° Tw	ı gal.
Water	Ι ,,
Copperas	IO OZS.
Starch	3 lbs.
Boil and add—	
Nitrate of iron, at 80° Tw	I gill

When printed the goods are allowed to hang for a few hours, then winced in a free flow of water, then again in chalk water; next in water again, and next in bichrome, at 40° Tw., in case of greens and yellows. Lastly, wash and dry.

Eleventh Style.-Pigment Printing.

This style has in the last few years undergone a great development. When first introduced, pigment colours had a heavy, opaque, dull effect, and were, besides, very liable to crack and peel off. These drawbacks have now been overcome, and designs are now executed in this style which have all the lightness and brilliance of colours formed on or within the fibre, whilst in point of solidity and permanence they leave little to be desired.

The first fixing agent selected was a solution of caoutchouc, in coalnaphtha, which was worked up with the pigment to be applied to a proper consistence. The naphtha was then driven off by the steaming-process, when there remained the colour cemented to the cloth by a thin film of caoutchouc. This process produced permanent results, but the evaporating naphtha became the cause of frequent and serious accidents. A variety of mixtures of drying oils and resinous matters—in fact varnishes—were also tried. The effects were generally heavy, resembling a spot of oil paint deposited upon the goods; the oil was liable to spread, producing a grease spot around the design, and the mixture not drying with sufficient rapidity, smearing was a very common result.

The principal vehicles now used for pigments are albumen, casein (lactarine), and gluten. Concerning the preparation and properties of these organic mordants information will be found in Chapter X., p. 80.

It must be remarked that the albumen of blood is coming more and more into use as a substitute for egg-albumen. The separation of albumen from

blood is effected as follows: - The fresh blood is collected in circular, flatbottomed basins with perpendicular sides, 14 inches in diameter and 4 deep, and containing about 2 gallons. In these the blood is let stand, without stirring, for two to six hours until coagulated. Filters are provided similar in form to the coagulating basins, but rather wider. Their bottoms and sides are pierced with holes 21 inches in diameter. These filters are lined with a dense, compact cotton or linen cloth. The serum is first decanted into the filter. The filtered serum is received into a depositing vessel. This has in its bottom a hole fitted with a cork through a perforation, in which a glass tube slides up and down. As long as the serum is not perfectly clear the upper mouth of this tube is kept above the level of the liquid, but when all subsidence is at an end, which may be in twelve to fourteen hours, the tube is drawn down so that its upper end comes below the level of the serum. By gradually sliding the tube downwards as required the serum, as far as clear, may be drawn off with even less disturbance than by a syphon. The clear serum is evaporated down to dryness at a very gentle heat, and may serve instead of egg-albumen for fixing light and bright colours.

The clot is next thrown upon the filter and cut up into small pieces. The coloured serum which runs through is not mixed with the clear, but is received by itself into the subsiding vessel, and treated in the same manner as described above. Its clearest portion is likewise evaporated to dryness, and serves for fixing dark and heavy shades. The blood of five oxen yields 2 lbs. of dry, colourless albumen. That of twenty sheep or thirty-four calves pro-

duces the same quantity.

The majority of the pigment colours used in this style have been already described (see p. 150), but we have yet to notice certain brown and black colouring matters.

Among these are-

Several metallic sulphurets.

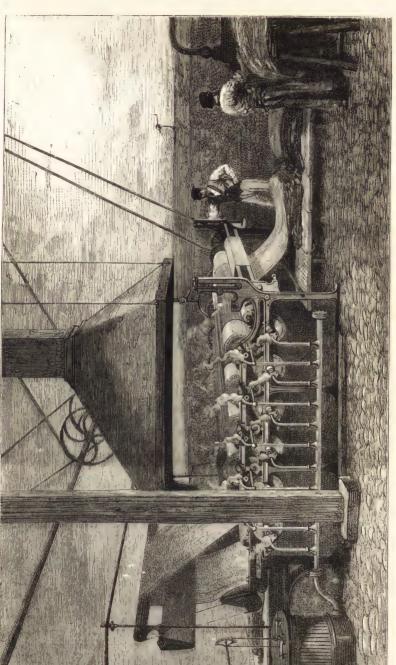
Brown oxides and Vandyke brown.

Substances, such as Umber, Terra de Sienna, Cologne earth, &c.

Lampblack.

The black or brown metallic sulphurets have been occasionally applied to tissues. Among the methods of fixing them may be mentioned the impregnating of the tissue with a soluble metallic salt, precipitable by sulphuretted hydrogen. The pieces are first passed into a solution containing solutions of lead, &c., and then are placed in an atmosphere of sulphuretted hydrogen; or the salts of such metals as lead, copper, mercury, cadmium, mixed with hyposulphite of soda, are printed on the tissue, and the latter steamed; the hyposulphite becomes decomposed into sulphate, and a sulphide of the metal is fixed.

Although lampblack is not used as a pigment to produce blacks, it is occasionally employed for solid greys. The lampblack is, previously to use, thoroughly purified by washing with caustic soda-lye to remove empyreumatic matters, and is next generally mixed with its own weight of ultramarine to obtain, by fixing with blood, a good grey; or it may be used with ochre, chrome-yellow, and other similar substances to produce various shades. Lampblack grey resists strong chemical reagents. Its use is more general



DRYING APPARATUS.





Guignet's Green and Chrome Green, Chrome Black and Dichromate of Lead.

abroad than in this country, for the reason that greys can be produced more cheaply by other means.

A fine argentine effect may be produced by blocking in zinc powder thickened with albumen. The pieces are then dried, steamed, and worked in a very neutral solution of protochloride of tin. The tin is thus reduced to the metallic state, and deposited in place of the zinc. The goods are then washed and well calendered to bring out the metallic lustre. The effect may be varied by substituting for the chloride of tin a very neutral solution of nitrate of copper, when that metal will be deposited instead of the zinc.

The three annexed specimens illustrate the pigment style in combination with other styles.



ULTRAMARINE BLUE, CHROME BLACK, AND DICHROMATE OF LEAD.

The darker green is a mixture of chrome green (Guignet's) and aldehyd green; the pale green is chrome green alone. The black is composed of logwood liquor, iron liquor, and red liquor. The orange is dichromate of lead. The greens and orange are fixed with albumen thickened with gum tragacanth. After printing the pieces are steamed for an hour.

The blues, dark and light, are ultramarine; the orange, dichromate of lead, all fastened with albumen and thickened with gum tragacanth. The black is chrome black, a mixture of logwood liquor, bark liquor, with chlorate of potash as an oxidising agent, and chrome liquor (acetate of chrome) as a mordant, and thickened with starch and gum. After printing the pieces are steamed for an hour.

The dark and light purples are mixtures of ultramarine and vermillion; and the yellow is chrome, all mixed and fixed with albumen, and steamed after printing.



ULTRAMARINE AND VERMILLION AND CHROME.

The next two specimens show a combination of pigment colours with madder-work. The blue in the first of these is ultramarine, the yellow a chrome-yellow, and the green a chrome-green, fastened with albumen, and subsequently steamed from thirty minutes to an hour. The black is a steam chrome-black, consisting of logwood and bark liquors oxidised with chlorate of potash, with acetate of chromium for a mordant, and thickened with gum and starch. The red is extract of madder, applied in the usual manner by printing on a mordant "colour" of acetate of alumina.

In the next pattern the slate colour is a pigment, carbonaceous grey, fixed as above directed. The black, green, and yellow are produced in manners similar to those in the preceding specimen, and the two shades of red are also produced with extract of madder. The mordants, thickenings, and manner of application are the same stops those just described.



ULTRAMARINE AND MADDER EXTRACT.

The pattern on p. 644 shows a combination of red, pink, orange, blue, green, and black colours. The red and pink are again extract of madder, the difference in depth of shade being produced by printing on mordants "colours" of different strengths. The black is a steam-chrome black, whilst the remainder of the colours, green, orange, and blue, are pigments mixed with albumen and steamed after printing.

The first pattern on p. 645 shows similar colours upon a pale green ground. The light and dark red, the deep green, the orange, the black, and the blue are first of all produced by the methods recently described, printed, steamed, and washed off. The entire piece is then "padded," that is printed all over with a pale green colour and steamed again. This method of working impairs the effect of the blue, red, and pink exceedingly little.



CARBONACEOUS GREY, WITH CHROME BLACK, CHROME GREEN, CHROME YELLOW, AND EXTRACT OF MADDER.

The second pattern on p. 645 shows the production of chrome-orange in light and dark shades, not by means of a previously-prepared pigment, but by the production of sub-chromate of lead in or upon the fibre itself. For a dark orange the brown or grey sugar of lead thickened with starch is printed on, whilst for a light orange a white sugar of lead is taken, and the thickening is gum. The calico, before printing, is prepared with a solution of sulphate of soda or sulphate of magnesia (Epsom salts). The thickened solution of sugar of lead is next printed on; after which the pieces are passed through a cold solution of sulphate of soda, and then through "sours" (very dilute sulphuric acid). They are next washed and then "raised" in the so-called orange vat for three to five minutes at a boiling heat.

The orange vat is made up with bichromate of potash, to which an excess of caustic lime has been added. Caustic soda may be substituted for caustic lime. The goods are next washed, and may then be passed through cold lime-water to clear the whites.



Extract of Madder, Red and Pink, with Chrome Orange, Green, Ultramarine Blue, and Chrome Black. (See p. 643.)

In addition to the receipts for aniline blacks, pp. 213 to 215, the following may be useful:—Cordillot employs—

I. As Thickener.—
Wheat-starch 10 kilos.
Water 24 litres.
Gum-water (1.2 kilos. per litre) 4 ,,
Tragacanth-water (65 grms. per litre) 6 ,,
2. As Oxidising Mixture.—
Thickener, No. 1 17 litres.
n which dissolve—
Chlorate of potash goo grammes.
After cooling add—
Ferricyanide of ammonium 2.6 kilos.



GREEN PADDED GROUND, WITH DESIGN IN MADDER, RED AND PINK, CHROME ORANGE, GREEN AND BLACK. (See p. 643.)

3. Solution of the Aniline Salt .-

Of the above thickener	 8 5					17 litres.
Hydrochlorate of aniline	 	b 0	B, B	b =	0.01	2.4 kilos.
Tartaric acid	 					500 grms.

For printing, equal parts of the oxidising mixture and of the aniline solution are mixed together.

Each of these mixtures can be preserved separately for a fortnight, but when once mixed they cannot be kept for more than thirty hours. The goods after printing are aged, washed, raised in a weak solution of chromate of potash, and then passed through a weak soap bath.



CHROME ORANGE, LIGHT AND DARK. (See p. 644.)

This mixture does not attack the doctors, but the black produced is less intense than that obtained by Lightfoot's process, and the price is a little higher. Cam. Keechlin replaces the ferricyanide of ammonium by ferricyanide of potassium and tartaric acid, and ages at a temperature of 50° to 60° C.

Lauth uses the following mixture:-

Tragacanth mucilage	 	 	 	1/2	litre.
Torrified starch	 	 	 	650 g	rms.
Water	 	 	 	950	9.9
Chlorate of potash	 	 	 	150	1.9
Sal-ammoniac	 	 	 	50	7.7
Hydrochlorate of aniline	 	 	 	400	17
-then hand he incornerates					

On the other hand he incorporates-

Wheat starch

1 1 0 1 1			4	Part 1		-
Water	 	 0.0			 250 ,,	
Sulphide of copper	 	 			 150 ,,	
TY HELLE DELICATION	 	 			 2	

When required for use the two are mixed together. The pieces are aged at 20° to 30° C.

The sulphide of copper is prepared by precipitating a solution of sulphate of copper with sulphide of sodium.

Müller prepares a black for printing as follows:-Dissolve-

Water		0.0		 			& litre	
Chlorate of potash				 			20 grms.	,
Sulphate of copper			* *	 	• •		30 ,,	
Sal-ammoniac				 			16 ,,	
Hydrochlorate of ani	iline			 * * "		• •	40 ,,	

The mixture is heated in the water-bath to about 60°. After two or three minutes the solution swells, and readily boils over. If, after the lapse of several hours, the thick mixture is not an intense black, it is once more heated to 60° C. The resulting paste is exposed for two days to the open air, then washed on a filter long and carefully, until no more saline matter can be discovered in the filtrate. A black of a more blue shade is obtained by using, as final wash-liquor, I litre of water in which 20 grms. of soluble aniline blue have been dissolved. It is thickened with albumen, of which it requires a large quantity, printed, and well steamed.

Lightfoot's method of applying aniline black to animal fibre, or to mixed fabrics, such as delaines, &c., is described as follows, in his Specification of September 11th, 1865 (No. 2327):—" For mixed goods I wince or steep them in a solution of hypochlorite of lime,—or a mixture of hypochlorite of lime, hydrochloric acid, and water,—for the purpose of preventing the deoxidising properties of the animal fibres and substances. When the wool or animal substance is thoroughly oxidised to its maximum, and in a fit state to receive the aniline black, it may be known by the following simple test:—Take a dilute solution of permanganate of potash in two test-tubes, and into one put a piece of the oxidised wool, and into the other a piece that has not been oxidised, and apply a gentle heat; the solution containing the one that is in a fit state to receive the aniline black remains pinky, but the other is decolourised immediately. The proportions for preparing the wool are about as follows:—I take for every pound of cloth, wool, yarn, silk, delaine, feathers, or animal substance (well cleaned), 6 gallons of water at about 100° F., 21 ounces by weight

of hydrochloric acid of commerce, and I pint of hypochlorite of lime in solution containing I lb. of hypochlorite of lime to the gallon. I keep the goods in this solution for from twenty to thirty minutes, or until the wool becomes quite yellow; I then wash well in water, and dry. The chlorodising or oxidising sufficient for ordinary colours is not applicable to aniline black, and a point of oxidisation or chlorodising is required which would not be advisable to give to fabrics intended for ordinary colours. In dyeing coburgs and similar goods the present processes involve two operations. I avoid this twice dyeing by preparing the mixture of cotton, wool, silk, or other animal substance, as above, so that they will both take a black dye at one and the same time. I steep or pad the goods, either before or after drying, in the following dye:—I gallon of water, 4 ounces chlorate of potash, I2 ounces chloride of aniline crystals, 6 ounces sal-ammoniac, 2 ounces sulphate of copper. I then dry the goods at as low a heat as possible, and age for two or three nights in a moist room at from 76° to 80° F., and when the colour is



ANILINE-BLACK, WITH MADDER-RED AND CHROME-ORANGE.

thoroughly developed it becomes an intense myrtle-green, almost black. It raise the goods either in water or any weak alkali, or in a weak cold solution of neutral chromate of potash, which I use in preference; and if a brownish-black is required, the goods may be subsequently dyed in a weak hot solution of orchil or cudbear. When the prepared cloth is used for printing, I print on the aniline black colour, as described in the Specification of my former Patent already referred to, and dry and age in a warm moist room, and raise in weak alkali as before. I then pass the goods through a warm solution of sulphite or hyposulphite of soda, or a solution of any suitable deoxidising agent, to improve the whites; or the goods may be passed through Mr. Thom's sulphuring apparatus. It is preferable after sulphuring to repass the goods through a weak alkali."

The above pattern, printed by the late Mr. J. Lightfoot, of Accrington, is an interesting specimen of the effects produced by combining aniline black

with other colours. It is obtained as follows:—For the red a mordant is used composed of red liquor, at 12° Tw., thickened with 2½ lbs. of flour per gallon. Cool, and add per gallon 4 ozs. of muriate of tin crystals.

For the orange:—
Nitrate of lead 4½ lbs.
White sugar of lead $4\frac{1}{2}$,,
Water 3 gal.
Dissolve, and add—
Gum Barbary, 6 lbs. per gallon 3 gal.
For the black:—
Sulphide of copper paste
Colour as below
To make the chlorate of ammonia:
Tartaric acid
Dissolve, and add gradually—
Sesquicarbonate of ammonia
Mix gradually, and add—
Chlorate of potash 8 lbs.
Dissolve, and stir for ten minutes. Let stand till cold, and filter. Wash the
precipitated tartar with 6 quarts of cold water. This should yield 6 gallons of clear chlorate of ammonia liquor.
To make the colour above referred to thicken this with British gum, 36 lbs.
(or a mixture of British gum and starch). Heat to 150° F., let stand till cold,
and add—
Aniline oil 4 quarts.
Best muriatic acid (34° Tw.)
Mix well together.
For the sulphide of copper:—
Flowers of sulphur 2 lbs. 2 dz
Caustic soda (70° Tw.)
Stir well till dissolved without heat, and add it to—
Sulphate of copper 10 lbs.
Boiling water 20 gals.
Wash till neutral to test-paper, and filter till the bulk of the pulp is reduced
to I gallon. Print, and hang in a room at 70° F., with about 8 or 9 degrees
of difference between the wet- and dry-bulb thermometers. Age till black,
and pass through ammonia-gas. Hang in a cool room for a few hours, and

then pass through the following solution at 160° F.:-

Phosphate of soda

.

2 lbs.

I oz.

ı gal.

Sulphate of soda

Water

Wash, and second dung twenty-five minutes at 130° F.

Water	 	 	 	 100 gals.
Sulphate of soda	 	 	 	 2 lbs.
Phosphate of soda	 	 	 	 I OZ.
Solid cow-dung	 	 	 	 4 quarts

Wash, and dye with 13 lbs. madder per piece. Wash, pass through chloride of lime at 1° Tw., then through steam-chest, and wash. Dry, and steam for thirty minutes at 2 lbs. pressure. Wet, soap-wash, and pass through weak sours (1 part of oil of vitriol, at 170° Tw.) to 1000 water, at 60° F.) for six minutes. Wash, and pass through chloride of lime as before. Wash, dry, and raise orange in the usual way—first in bichrome alone, and then in bichrome and lime at 212° F. Wash well, and pass through chloride of lime as before. Wash and dry.

Paraf proposes the following process:-" Instead of using chloric acid combined with potash I combine other bases which form salts more soluble or less liable to crystallise, as soda, oxide of lead, barytes, strontian, lime, magnesia, or similar bases. As the chloric acid of the chlorate ought to be set free to enable it to oxidise, it will be easily perceived that I can liberate the base more easily from the chlorates of barytes, lead, strontian, or lime, than from chlorate of potash, by means of acids forming insoluble salts with the bases herein named. I have already applied a reaction of potash to facilitate the decomposition of chlorate of potash, and thus dispense with a great part of its defects. Instead of decomposing by the usual acids,—as oxalic, tartaric, nitric, and similar acids,—I decompose by hydrofluosilicic acid, which gives a salt of potash nearly insoluble, sets the chloric acid free, and prevents the making of crystals. In consequence of the greater solubility of the chlorate, and more complete setting at liberty of the chloric acid, I can put a larger quantity in contact with the substances to be oxidised, and I obtain more complete oxidation for steam-colours, such as catechu and the aniline-blacks, and similar colours. I obtain good results for aniline-black by using the following proportions, which I will call 'black liquor's: - I part chloride of aniline, I part hydrofluosilicic acid at 6° Tw., and Io per cent of protochloride of iron dissolved in the aniline and acid. To save the greys the cloth is prepared in a solution of chlorate of soda, at 6° Tw.; then print on the following colour: -2 lbs. of aniline-black liquor, 3 lbs. of water, 2 lbs. white starch, 2 lbs. gum-dragon paste, 1 lb. brown British gum, 7 ozs. lamp-black. Boil well together, and cool down. Age in a cold room for one or two days, but if pressed for time the black can be produced in a few hours by running once or twice through an ageing-machine. If saving the greys is no object the cloth does not require any preparation, and the soluble chlorate can be given in the colour and printed together upon the cloth. I use the following proportions: -First, 2 lbs. black liquor, 3 lbs. water, 1 lb. starch, all well boiled together; second, 6 lbs. chlorate of soda at 20° Tw., 2 lbs. starch, 2 lbs. brown gum paste, 2 lbs. gum dragon. For the colour I use I part of the first mixture to I part of the second, and mix them cold. I can add, also, to a colour containing a small quantity of chlorate of potash, other chlorates of greater solubility than chlorate of potash, and the result will in all cases be better

^{*} An ill-chosen name, since it already denotes the acetate or pyrolignite of iron.

than with chlorate of potash alone. When I impregnate a fibre or pad fabrics in a soluble chlorate which I dye in or print upon with a colouring matter to be oxidised, as e.g. in the aniline black, when I want to secure the greys, I can hasten the oxidation by adding to the colouring matter to be oxidised, or in the aniline black colour, 2 or 3 per cent of a salt of oxide of iron, copper, chrome, or manganese. I also use chloric acid, combined with aniline or its homologues, for the production of black or grey colours. I decompose sulphate, oxalate of aniline, or similar salts, with chlorate of barytes, lead, lime, strontian, so as to produce by double decomposition chlorate of aniline or its homologues, which, printed or dyed upon fabrics or yarns, produces fast blacks or greys by ageing; and in this case I find also an advantage in adding to the aniline 2 or 3 per cent of a salt of iron, copper, chrome, or manganese. Animal matters do not take easily colours formed by oxidation. I surmount this difficulty by fixing in the fibre metallic oxides, such as copper, alone or combined with chrome, and then the animal matter takes aniline black colours. I find an advantage in preparing the animal matters which have to be dyed or printed with aniline black in the following mixture:-- I lb. sulphate of copper, \frac{1}{2} lb. chlorate of soda, \frac{1}{2} lb. bichromate of potash, and r gallon of water."—(Specification No. 2859, November 6, 1865).

In another patent the same chemist recommends the use of-" Insoluble binoxide of chromium, or insoluble or soluble chromate salts capable of evolving chromic acid, either slowly, in the presence of water or certain acids or alkalies, or simply by ageing or steaming; and I find it of great use in the production of aniline and its homologous black or grey colours, in which I mix a salt of aniline and the brown binoxide of chromium, either alone or in conjunction with a chlorate, and such mixtures printed upon cloth produce fast aniline black by ageing. The following proportions have given me very good results: - First, 12 ozs. chloride of aniline, 3 lbs. of water, and 1 lb. of starch, boiled together; secondly, 8 ozs. of brown binoxide of chromium in paste, and 4 ozs. of chlorate (of what base the patentee does not state), to I gallon of thickening. The colour for printing is a mixture of equal parts of these two compositions. If I want to dye or print very heavy objects, I can easily produce the necessary quantity of binoxide of chromium in the fibre by padding or dyeing first in a solution of a sulphate or chloride of chromium, and then passing the goods through a solution of monochromate of potash; then dye in a salt of aniline. The chlorate hastens the production of the colour, but the binoxide of chromium and the salt of aniline can be used alone, and give very good blacks; but in this I find an advantage in introducing in the colour from 3 to 5 per cent of arsenic acid, which in this case assists the decomposition of the binoxide of chromium." - (Specification No. 1174, April 26, 1866).

Murexide Purples.

Like the aniline blacks, the murexide shades do not fall naturally under any of the above great styles. Upon cotton the following formula gives a deep shade:—

Gum-water		 	 	 	 I litre.
Nitrate of lead		 	 	 	 400 grms.
Crystalline murer	kide	 	 	 	 I grm.

For light shades dilute the above with gum-water containing 100 grms. nitrate of lead per litre. After printing, the goods are hung up for a few hours in moist air. They are then passed, for a minute or half a minute, into a chest, the air of which is strongly impregnated with ammonia, and next passed into a bath containing 2.5 kilos. of corrosive sublimate per 1000 litres of water. Here they are left for twenty minutes, then washed in flowing water, and passed anew into a bath containing—

Wash, and dry. If the pieces, after drying, are passed through a weak alkaline bath, the colour becomes more violet.

Operations Accessory to Dyeing.

Although the process of bleaching has been described in an earlier portion of this work (see pp. 44 and 87), there are a variety of subsidiary operations, both before and after dyeing, in the strict sense of the term, which require explanation. As a preliminary, it will be needful to glance briefly at the different states in which textile materials are submitted to dyeing, and which have been only incidentally mentioned.

Cotton is very rarely dyed in the unspun state, as cotton-wool. It is chiefly dyed as yarn or spun thread, either in the hank or-in some cases-in the cop. The latter process, where practicable, is economical, as saving the time and labour required for forming the yarn into hanks; but to cause the mordants and dye-liquors to penetrate through a compact cop, so that the colour produced may be full and even, is very difficult. Cotton is comparatively rarely dyed in the woven state. Wool is operated upon by the dyer in a greater number of states. Very large quantities are dyed in the original, unspun, state: this is the case with the wool intended to be worked up into superior qualities of broadcloth. The dye, under these circumstances, has full facility for acting thoroughly upon every fibre: hence wool-dyed colours are generally considered the fastest, and the goods, other things being equal, fetch a higher price than such as are dyed in the piece. In consequence, stratagems have been devised for giving to piece-dyed doe-skins, &c., the appearance of having been dyed in the wool. In piece-dyed goods the listings are, naturally, of the same colour as is the body of the piece. If, however, there be applied to the listings some solution which may discharge the dye, and leave them either white or of a shade differing from that of the body of the piece, purchasers are led to suppose that the cloth has been dyed in the wool.

Wool-dyeing, besides superior fastness and penetration, has the advantage in evenness. Should any slight inequality, either of depth or of tone, occur, yet when the whole of the wool has been "scribbled" together such defects disappear, and the surface of the woven cloth will be found to exhibit a colour absolutely alike in all parts. To counterbalance these advantages great care is required that the pieces may not become soiled in any of the operations subsequent to dyeing. The chief practical difficulty in wool-dyeing is to prevent the mass from becoming felted together, so as to be unfit for carding and spinning. In wool-dyeing care should also be taken to present the wares in a suitable form. If ground or chipped dye-woods, orchil-paste, &c., are used.

the fragments become entangled among the wool, and can only be removed—if at all—by very tedious washing. Hence the woods, &c., should be applied in the state of liquid extracts.

A further very large quantity of wool* is dyed in the state of yarn. Almost all the wool used in carpets, hosiery, shawls, table-covers, dress-pieces, and all those goods in which the Jacquard loom shows itself a formidable rival to the printing-machine, is yarn-dyed. Wool is sometimes also dyed in the state of "slubbings" or "slivers." These are long masses of wool, which, by drawing out and twisting, become converted into yarn; they require, in dyeing, the same precautions as loose wool. Piece-dyeing holds a very prominent position as regards woollen and worsted goods. By far the greater part of stuffs, whether consisting of "all wool" or of a worsted weft and cotton warp, are dyed in the piece. So, likewise, is the bulk of the cloth made in the present day. The piece-dyer has certain peculiar difficulties to encounter: the first of these is the possibility of the dye attaching itself more strongly to one part of the surface of the cloth than to another. If this once takes place the piece has a more or less cloudy or spotty appearance, which is very difficult to remove, and which cannot exist without at once betraying itself. There is especial danger of this unevenness with dyes which have a very powerful affinity for the fibre, and which are consequently apt to seize hold, in excess, of the first portion of the piece that enters the dye-beck. To prevent or lessen this tendency certain substances are used called levellers. One of these is sulphate of soda, Glauber's salt, or sal-enixum, called by many dyers Sally Nixon. This salt is added to many dye-mixtures, and seems to lessen the affinity of the colour for the cloth to such a degree that instead of being rapidly and irregularly deposited upon the surface-it interpenetrates the whole equally, and produces an even or "level" shade.

With the aniline colours the risk of irregularity is very great, especially on goods woven from fine, soft wools. If any particles of the dye have escaped perfect solution, and remain suspended in the beck,—if the methylated spirit frequently used as a solvent has partially evaporated, leaving some of the colour in the form of a bronzy scum on the surface,—or if the liquid has been worked up into a froth or "flurry" by the rapid passage of the pieces through the beck,—spots and stains are almost inevitable. To prevent these inconveniences glycerin may be used in dissolving the dye, or may be subsequently added to the bath. It does not allow the colour to separate out, and prevents bronzing and "flurry." With magenta, small quantities of white soap are used by some dyers—an addition which levels the colour, and gives a slightly redder tone. A dcccction of Panama bark (Quillaja saponaria) is sometimes added to the dye-beck, with good effect, for the same purpose. Pieces spotted and stained, "flushed" with aniline colours, may be considerably improved by being winced in this decoction.

Panama bark is also used for another purpose, which it may not be out of place to mention here. If it is desired to produce upon woollen or worsted goods the purest and most lustrous whiteness,—whether for sale in that state as "double-stove whites," or for being dyed particularly light and brilliant shades, such as light roses, light greens, peaches, pale violets and blues, &c.,

^{*} The distinction between wool and worsted is, from a tinctorial point of view, unimportant.

—after being repeatedly sulphured (see p. 88) and washed in the usual manner, the fabric receives a final washing in the decoction of Panama bark, which leaves it more lustrous to the eye, and softer and more kindly to the touch than the best-balanced and most emollient soap. Some good practical authorities maintain that where quality is of more importance than cheapness the process of sulphuring should be performed,—not with the fumes of burning sulphur, but with a solution of the bisulphite of soda (leucogene), or, better still, bisulphite of magnesia. As to the mordanting power ascribed to these bisulphites, further experiments are wanting.

Returning to the prevention of irregularity in piece-dyeing, in case of colours whose affinity for the fibre is very strong, it is often found prudent to dissolve at the outset merely a part of the dye needed to bring up the goods to the shade required, and to add the rest by degrees. A good mechanical precaution to ensure a level shade is to wince the pieces at first with great swiftness. The wetting the pieces with water previous to dyeing is also a point of importance. If any portions of the goods have escaped being thoroughly moistened, or if they are in the least degree greasy, soiled, or abraded, irregularity is certain.

Another essential point in piece-dyeing is thorough penetration of the colour, so that, if a small portion be torn or cut off, the section or tear may bring to light no undyed filaments. If the cloth is not dyed through and through it will, after a little wear, begin to exhibit a greyish reflection, and complaints will reach the dyer that his colours "wear off." Cloth that is not dyed through generally displays a correlative fault; the colour is deposited loosely on the outside,—"plastered on," as it is technically called, and is hence deficient in lustre.

Rag-dyeing is a branch requiring more skill and judgment than the outside public are aware. Woollen clippings and rags, after some rough sorting as regards colour, are re-dyed preparatory to being converted into shoddy and remanufactured. As these rags have been dyed before, the production of the new shade required is attended by the discharge or alteration of the old. From the nature of the case it is important that these changes should be effected with the smallest possible outlay in wares. To take a very simple case—the conversion of black rags, dyed with an iron mordant and logwood, into claret. To strip the black dye from the rags, rendering them white or nearly so, and to produce upon them a claret shade, as would be done upon new material, would be tedious and costly; but the end is gained simply by boiling the black rags with water to which a suitable proportion of claret spirit (p. 526) -a preparation of tin-has been added. On the fibre is a black compound of oxide of iron and of the colouring matter of logwood. The chloride of tin attacks the iron, and removes it by reason of its superior affinity at once for the wool and the colouring matter. What remains on the fibre is then a claret-coloured compound of oxide of tin with the logwood. Thus the re-dyeing is effected without the use of any fresh dye-ware, one mordant having been merely substituted for another. Evenness of colour is not insisted on in case of rag-dyeing, since, when the material has been torn up into shoddy, all its irregularities disappear.

The re-dyeing of worn garments (job-dyeing) may be classed with piecedyeing, and offers all the especial difficulties of the latter, heightened by the circumstance that the irregular abrasion of different parts of its surface renders the attainment of a really level shade impossible.

One of the subsidiary operations applied to stuffs about to be dyed in the piece is singeing. The object of this process is the entire removal of all roughnesses and projecting fibres, so that the stuff may exhibit a perfectly smooth surface. This can only be effected by a rapid combustion, so perfectly under control that the down may be entirely burnt away without the body of the tissue being in the slightest degree weakened or discoloured. This was formerly done by passing the goods with great velocity over a convex plate of cast-iron, heated to a very high temperature. It is now executed, in preference. by the aid of burning coal-gas. One of the best arrangements for this is Tulpin's singeing-machine (Pl. VIII.). The use of gas was at first greatly restricted, in consequence of a defect which seemed insurmountable. As the pieces moved above the points of the flames which burnt the down, the act on was not sufficiently limited to the surface, but extended to the filaments in the interior of the tissue, which was thus rendered thinner, and its value was reduced. Tulpin remedies this defect by employing, not the point of the flame, but its lateral part, along which he causes the stuffs to graze. His machine is so contrived that the operation can, at will, be repeated twice on each side. The steadiness of the flame is secured by means of a ventilator which draws off the products of combustion. A smaller ventilator sends in air, and mixes it with the coal-gas in sufficient proportion to produce a blue flame as in the Bunsen burner, giving out heat rather than light, and completely free from smoke. In this manner the danger of staining or blackening the pieces is completely obviated. This singeing-machine may be advantageously used in preparing calico for printing.

Another important operation is "crabbing." Before stuffs can be dyed, all dirt, grease, and the dressing used by the weaver, must be completely removed. The pieces are generally first passed through hot water, to dissolve and remove size or stiffening. They are next treated with hot lyes of soap, carbonate of soda, and liquid ammonia, to remove all fatty and resinous matters. Every trace of soap and alkali is finally washed out, by rinsing in abundance of water. The apparatus used resembles that figured on p. 306 (Fig. 22).

The manipulation—" working or turning"—during the act of dyeing itself is conducted in different manners, according to the nature of the goods. In wool- and rag-dyeing the dyer's pole is still employed to turn the material operated upon; but in piece-dyeing there is fixed over every beck or cistern a roller or wince, which can be turned by hand, or, as is more common in large modern establishments, by steam- or water-power. Round this roller the pieces are wound, and, as it revolves, they are alternately let down into the liquid and drawn out again, the dyer taking care that they do not get entangled, —which sometimes happens with thin goods,—and that they coil and uncoil evenly.

After the completion of the dyeing—properly so-called—the pieces are, as a rule, saturated with an excess of uncombined colouring matter, from which they require to be freed by copious washing. This was formerly effected by suspending the goods in a clear running stream. Since in manufacturing districts the rivers are now more adapted to soil than to cleanse anything, this primitive method of washing has given place to mechanical arrangements

such as that represented in Pl. IX. The pieces, on leaving the dye-beck, enter a large tank of water, where they are well agitated: hence they pass between two cylinders under a torrent of water discharged upon them from above; they next descend into a narrower tank, into which water falls from a wide pipe; they are then passed between a second pair of cylinders, still exposed to a copious descending shower of water.

The process of drying is conducted in various manners, according to the nature of the goods. Cloth is generally stretched out on "tenters" (extenders) in the open air, or in large sheds heated by steam-pipes. Certain colours very susceptible to the action of light, such as safflower shades on any kind of material, are best dried in the dark, by means of a current of cold air driven over them by means of a fan. Worsted and mixed stuffs, such as merinos, coburgs, delaines, &c., are dried by passing over rollers heated by steam, as shown in Pl. X.

With the modern rage for apparent cheapness the process of finishing has grown in importance. Goods, both white and coloured, depend to a great extent for their appearance, and even for their body, not so much upon textile fibres—whether animal or vegetable—as upon a variety of dressings, finishings, and weightings, for which the wool or cotton serves merely as a kind of framework. Gums, Iceland moss, starches, glue, sulphates of lime and baryta, Epsom salts, and chloride of magnesium, dexterously mixed and introduced, hide a multitude of deficiencies, and convert a weak, straggling, canvass-like network into a smooth, full, and compact article—until it has paid its first visit to the wash-tub, when the truth is revealed. These additions are made most largely to cotton goods: woollen cloths are weighted to some extent with the chloride of magnesium, which—from its high specific gravity, its power of attracting moisture from the air, and its want of action upon colours—receives the preference.

Stuffs, previous to finishing, are moistened with an extremely fine shower, produced by allowing water to descend through a sieve of silk. They are then passed over the finishing-machine shown in Pl. XI., consisting of three hollow cylinders, the temperature of which can be rapidly raised or lowered. This operation requires a very considerable amount of skill and experience on the part of the workmen, and on its correct execution the appearance of the goods greatly depends. The last process to which stuffs are subjected in dyeworks is hot-pressing. Between each fold of the piece is placed a layer of a smooth, elastic paper, made expressly for this purpose. At certain intervals plates of cast-iron, strongly heated, are inserted, and the whole is submitted to the action of the hydraulic press.

Influence of Light upon Colours.

In its action upon colours light has been compared to the Indian Trimurti, combining the triple functions of generator, modifier, and destroyer. In darkness we are told organic colours are not produced, whilst the more intense the light the more brilliant and varied are the hues developed. In support of this view a great body of facts may be brought forward. That the flowers, the fruits, the insects of tropical regions are more richly coloured than those of climates where the sun has less power is a truism. If we argue that the colours thus produced may be due, wholly or partially, to the higher

656

temperature of the torrid zone, we are met with the following phenomena:-The leaves and flowers of plants kept in dark places are pale and bleached in appearance, irrespective of the temperature to which they are exposed, as, for instance, the shoots of a potato kept in a dark cellar. The diurnal Lepidoptera of all countries are much more splendid than the nocturnal species of the same districts. The under surface of the wings of butterflies is often as gaily coloured as the upper. But it is as nearly as much exposed to light, both when the insect is flying and when it is in a state of repose. In moths, on the other hand, when the under surface is very little exposed to light, its colours are sombre and monotonous. Nocturnal beetles of the Lamellicorn order, such as the Geotrupidæ, exhibit dull and dark shades, whilst the Cetoniads, the diurnal members of the same order, might be characterised as animated jewels. Among birds and mammals the same general rule prevails; those of sunny climates are brighter than those of cold and gloomy countries; diurnal species are more gaily clad than the nocturnal, and in one and the same species the parts most exposed to light—the head, back, and shoulders -are more highly coloured than the belly, and, in birds, the sides where covered by the wings. The difference in appearance between the sunny and the shady side of a peach or an apple is well known, as also the circumstance that the stems of plants, green above the surface of the soil where fully exposed to light, are pale or colourless below, where the light is excluded. On the faith of these, and similar phenomena which do not require to be individually enumerated, the colouration of organic bodies is generally considered to be a direct result of light, increasing in depth and brilliance with its intensity, and fading away in its absence.

But there are, on the other hand, indisputable facts which must tend to modify this conclusion. In the vegetable world we find roots completely excluded, of course, from the light during the whole life of the plant, and yet coloured or even containing powerful colouring matters. As common examples we may cite the carrot, the Eschscholtzia, and madder, with its congeners. It has been often pointed out that that the timber of trees growing in cold climates is pale, whilst in the torrid zone deep colours are generated, as in the dye-woods, ebony, and others. But the heart-wood of a tree is certainly not exposed to any direct action of the solar rays. In the animal world it must be remarked that subterranean and nocturnal species cannot be indiscriminately pronounced to be pale, bleached, or etiolated. On the contrary, many of them, such as the Harpalid and Geotrupid beetles, certain spiders, &c., exhibit intense colours, such as deep browns or blacks. The common badger presents a striking exception to the rule that the upper or sunny side of animals is more deeply coloured than the belly. Two genera of moths, the Arctias and Catocalas, display colours as gorgeous as any butterfly-scarlet, crimson, rose, and blue. Yet these colours are almost confined to the hinder wings, which are completely and closely covered by the anterior pair when the insect is at rest, and are only unfolded on the night air when it is flying. Perhaps the most nocturnal quadrupeds are the Felidæ, yet amongst them we find some of the most gaily coloured species of mammalians. Again, though plants allowed to grow in darkness are devoid of their natural colours, animals do not, under the same circumstances, undergo a corresponding change. This has been proved by direct experiment. Caterpillars of Vancssa Io have been reared up in darkness, but when matured and transformed into butterflies they exhibited the usual colours of their species in undiminished brilliance. Nay, in the common course of nature, many insects pass their period of development in perfect darkness, and then suddenly emerge in the full splendour of their mature state. This, for instance, is the case with the Buprestids, with the Longicornes, the Curculionides, including the gorgeous diamond beetle. How, then, can it be contended that the colouration of such species is, in any direct manner, the work of light? If we found that the larvæ of brilliant insects were, as a rule, more exposed to light than those of dull and sombre species, or if, when arrived at maturity, the development of their colours were at all dependent upon the amount of light which they encountered, we might then entertain a different opinion.

With artificial colours and dyes the action of light is also very doubtful. Let us take the case of rosanilin: it will scarcely be conceded that this dye was pre-existent in the wood or other vegetable matter from which the coal originated. In its subsequent career in the mine, in the gas-works, and in the colour manufactory its exposure to light has been trifling indeed. Nor do any facts seem to indicate that either the quality of the aniline colours would be improved or the yield increased by the action of light during the various stages of its manufacture. We cannot, therefore, pronounce light to be exclusively or pre-eminently the direct colour-generating force; although that it indirectly promotes the development of colours in organic beings is extremely probable.

As a modifier and destroyer of colours the action of light is very manifest. Very few colours, natural or artificial, can be long exposed to direct sunlight without undergoing some degree of change, which may vary from a slight alteration of tone to total discharging. Every stage of this action may be seen in the vegetable world. Certain flowers, such as the wild rose, the blackberry, and nut-blossom, the wood-sorrel and the wood-anemone, are perfectly bleached by a few hours' exposure to sunshine. In other cases there is either a change from red to blue or from blue towards red. The former variation can be seen in the flowers of the mountain-heath (E. cinerea), which when overblown pass from their original rose to a violet. The second, or inverse, change may be seen in the corolla of many varieties of fuchsia, which is of a blue-violet shade when the flower first opens, but becomes redder and redder the longer it is exposed to the light. The changing colouration of the leaves of trees, as it gradually passes from the pale but bright tones prevalent in spring, to the full, deep greens of summer, and thence to the maroon, orange, yellow, and brown of autumn, is due in great part to the same agency. This may be proved by a simple and by no means rare phenomenon. When the leaves of a tree or bush are in their full autumnal colouration, a portion of one may often be found which has been doubled and fastened down by some caterpillar. The part thus covered from the light retains its ordinary green hue, whilst all the rest of the leaf is a maroon or reddish-brown. In the animal world the changes of colour produced by light are generally destructive. The distinction between fast and fugitive colours prevails, however, here, as well as in the products of the dye-house and print-works. Almost all the colours of quadrupeds and birds are fast, sustaining indefinite exposure to sunlight without modification. Among insects the colours of beetles and Hemiptera are, with the exception of a few non-metallic green and pink shades, permanent. Butterflies and moths, on the other hand, no matter how thoroughly protected against air, friction, or other mechanical injury, have their colours completely discharged in the course of a few years even by diffused daylight. Greens, lilacs, and pinks are here, again, the most fugitive, whilst yellows, browns, full reds, and all "metallic" or iridescent spots resist longest.

Whatever diversity of opinion may prevail concerning the part played by light in the development of colours and in their fixation upon tissues, there can be no doubt as to its influence when once the process of dyeing, printing, or painting is completed. In almost every case it is injurious. The action ranges from rapid destruction, as in the case of safflower pinks, magentas, &c., to gradual deterioration, as with royal blues, chrome blacks, &c. Few colours, indeed, do not show a distinction if a swatch be cut in halves and preserved, the one in darkness and the other in the light.

Nor is this action confined to dyed or printed tissues. The colours themselves, be they dyes or pigments, are also affected by exposure to light. Extract of indigo, if exposed to diffused daylight, gradually loses its blue colour, and is reduced to a faint yellowish green. Mordants also, especially the preparations of iron and tin, lose their affinity for the fibre, and are rendered worthless by even a short exposure to direct sunlight. This change is very marked with the mordant known as nitrate of tin or "bowl-spirits" (see p. 527). By sunshine it is rendered milky and turbid, a great part of the tin in solution is precipitated, and the remainder becomes useless. Cotton or woollen fibre worked in this spoiled mordant and then transferred to the dyebeck, takes only very flat, meagre, and uneven shades. The ordinary persalts of tin (crimson spirit, oxymuriate, &c.) are little changed in appearance by the action of light, but they do not work on the fibre, the shades ultimately produced closely resembling those obtained with a spirit which has been "fired" (see p. 529). This is not the only case in which the effects of light in dyeing processes agree with those of an elevated temperature. Safflower shades are discharged if dried in too great a heat, far below a temperature injurious to the fibre, just as readily as if exposed to direct sunlight.

Nitrate of iron, especially if intended for dyeing royal blues, should be kept in the dark until wanted. If this precaution is neglected the mordant becomes turbid, and the shades produced on the fibre are deficient in bloom and brilliance. This result is the more interesting, because solutions of iron intended for use in the manufacture of Prussian blue as a pigment are not injured by the sun's rays. Some practical colour makers, indeed, contend that the beauty of the pigment is improved if the materials are exposed to

light previous to precipitation.

Light is supposed to have an action upon madder from the time when the dried root is ground up and packed very finely in strong casks. The older manufacturers, especially in Zealand and Alsace, have from time almost immemorial considered that madder, while being ground and packed, should be withdrawn entirely from daylight. The custom of the Meestoven, as the drying and grinding establishments are called in Zealand, was to work by scanty lamplight. In modern times this precaution has been laid aside and the root is generally ground by daylight. There are, however, some persons possessing great practical acquaintance with madder (especially in Zealand) who maintain that the root ground in the dark is better—works better in the

cask, as they phrase it—than that ground in the daylight. The latter finds its way largely to the garancin manufacturers. An investigation on the changes which madder undergoes while in the cask was commenced some years ago. Samples were taken out of the casks with a suitable tool every ten days for two years, care being taken to have the casks (about 400 in number, each containing 750 kilos., and among them 100 containing madder ground by daylight) kept in a dark warehouse where the temperature, hygroscopic condition of the air, and the general state of the weather were taken into account. The series of experiments was unavoidably interrupted, but it was ascertained that there is good reason for preferring the madder ground in the dark.

The following table has been drawn up by F. V. Kallab. The samples were exposed to the sun during the months of July, August, and September, 1872. and were compared with corresponding samples carefully preserved from the action of light:

action of fight.	Influence of Sunlight.									
Dye-ware.	From three to eight days.	Three months.								
Indigo blue.	No change.	Much lighter.								
Copperas vat on cotton.	27 27	Greenish.								
Vat blue on woollens.	77 79	Pure blue but lighter.								
Extract of indigo.	Paler.	Very pale and greenish,								
Purple extract.	Rather paler.	Less bloomy and paler.								
Prussian blue.	Paler by day; recovers its former shade by night.	If rinsed in water in the evening the lost colour does not re-								
		return.								
Logwood blue.	Paler.	Grey; lilac shades nearly white.								
Aniline blue (?)	Much paler.	Very pale; light shades white.								
Nicholson blue.	Little change.	Paler and duller.								
22 22	29 79	Greyer.								
Weld yellow.	Unchanged.	Rather paler.								
Quercitron.	Paler.	Straw colour.								
Flavin yellow.	27	Nearly white.								
Berries, yellow.	Duller.	Dirty yellow.								
" orange.	Dirty orange.	Pale dirty orange.								
Fustic yellow.	Paler.	Dirty straw.								
Young fustic orange.	Much paler.	17 71								
	(Light shades, whitish.	Quite white.								
Turmeric yellow.	Dark ditto, straw.	Reddish.								
Picric yellow.	Orange.	Like dark young fustic yellow.								
Blackley orange.	No change.	Turns a little paler at last.								
Campo-bello yellow.	9 9 9 9	Pale reddish at last.								
Buff (iron).	11 19	No change.								
Chrome yellow and	99 99	Duller; greenish.								

orange.

Influence of Sunlight.

	Influence of Su	inlight.
Dye-ware.	From three to eight days.	Three months.
Annatto yellow.	Redder.	Bright.
Madder red (cotton).	No change.	Printed, paler; dyed,
		purer and brighter.
Alizarin, pure.	22 22	No change.
,, artificial.	99 79	22 22
Cochineal.	27 22	Rose, paler; scarlet,
		bluer; crimson, paler.
Ammoniacal cochineal.		Much bleached.
Red wood reds.	Dull.	Pale flesh colour.
Safflower red.	Paler in a few hours; much	Quite bleached.
	bleached in eight days.	
Saffranin.	Stands better than safflower.	39 39
Murexide.	Duller and paler.	Nearly ,,
Magenta.	99 99	Bluish, much bleached.
Chloronaphthalic acid.	Unchanged.	Turns flesh colour.
Orchil.	Duller and paler.	Light flesh colour.
Aniline violet.	Stands better than orchil.	Much bleached.
Alkanet.	99 93	Bleached.
Madder purple.	No change.	Scarcely changed.
", brown.	79 99	11 11
Catechu.	77 77	Yellowish and pale.
Phenyl brown.	;; ;;	Not darkened with oxi-
		disers, more in-
		tense; darkened,
	D 11	lighter & yellowish.
Compound browns.	Duller.	Tinht shades meal
T. 1'	On wool, lighter.	Light shades, wool,
Iodine green.	On cotton, bleached.	white. Dark shades, cotton,
	On cotton, bleached.	bleached.
Toding groom with pionic	Duller.	Dirty yellow green.
Iodine green with picric acid.	Dunei.	Dirty yellow green.
Extract of indigo with	Yellower.	Pale olive green.
picric acid.	Tellowel.	are onve green.
Ditto with fustic.	Less changed.	Pale and dull.
Vat-blue with vegetable		Bluer.
yellow.	11 11	Didei
Vat blue with chrome	Unchanged.	Duller.
yellow.	0	
Fustic and logwood	Duller.	Pale.
green.		
Guignet's green.	No change.	No change.
Schweinfurt green.	1) 1)	22 22
Stove whites.	" "	If with sulphur alone,
		lose merely the blue
		surface shade; if
		soap was present,
		turn yellowish.

Influence of Sunlight.

	Innuence of	Sumignt.
Dye-ware, French whites with	From three to eight days. Bluer.	Three months. Orchil quite bleached,
extract of indigo, orchil, and chloride of tin.		leaving a greenish white.
Logwood black.	No change.	Chrome, greenish; cop- peras, little change.
Aniline black.	27 17	Wool, no change; cotton, greenish.

CHAPTER IX.

DETECTION OF DYES ON VARN OR PIECES.

DYERS generally judge of the composition of any colour which they meet with, either by simple inspection or by certain routine processes which have been traditionally handed down from generation to generation. Even at the present day there are many dyers who believe that the colouring matters of commerce cannot be detected with certainty. Hence they employ the known reactions of tinctorial substances as little as possible. In order to show how far even a slight knowledge of chemistry will aid in the recognition of dyes, we give simple directions, arranged under the six heads of Black, Blue, Yellow, Red, Green, and Violet.

The apparatus employed is very simple. For steeping the tissues or skeins of silk, cotton, or wool, a small white porcelain capsule is needed, and for the application of heat a small iron tripod, with a spirit-lamp or Bunsen gas-burner. The white colour of the porcelain renders it easy to observe the changes of colour under the influence of reagents. In order to reduce portions of the tissue to ashes, a small platinum capsule or piece of platinum foil is used, which may be heated to redness in the flame until all combustible matter is employed and only the ash remains. The colour of the ash indicates the character of the dye, of which more below. It may be green, blue, grey, white, or red.

A. BLACKS.

these a kind of chestnut-brown. If exposed to bright sunshine they become greenish. If thoroughly burned they leave a greenish ash.

2. Logwood with Iron Mordants.—Dilute hydrochloric acid turns the swatch a cherry-red. The prompt application of a dilute alkali restores the black. Solution of bleaching-lime discharges the black, leaving a yellowish ground (oxide of iron). The cloth leaves a yellowish-brown ash.

3. Galls with Iron Mordants.—This dye is chiefly found on the better class of silks. Hydrochloric acid gives no immediate red colour. Bleaching-liquor discharges the black, leaving the iron ground as above.

4. Logwood with Iron on a "Woaded," i.e., Vat-Blue, Bottom.— Hydrochloric acid has no immediate action, but gives in a few minutes a dull purplish red spot. A mixture of hydrochloric and oxalic acids extracts a red liquid, and leaves a blue bottom. Nitric acid extracts a similar liquid, but leaves a yellowish-brown ground.

5. Aniline Black.—Strong hydrochloric acid gives no immediate change, but after a quarter of an hour the cloth will be found to have taken a greenish-yellow, while the liquid is an olive-brown.

6. Lamp-Black. - Cannot be discharged. Ash white.

B. BLUES.

The principal blue colours of which we shall speak are: -

- I. Logwood blue.
- 2. Prussian blue.
- 3. Aniline blue.
- 4. Indi o blue.
- 5. Mixed blues.
- 6. Ultramarine blue.
- I. We begin by placing a piece of the cloth to be tested in a solution of citric acid, or in hydrochloric acid treated with water.
 - a. The colour changes to red or orange. Logwood.
 - b. The colour does not change. (In this case any of the other three dye-wares may be present.)
 - II. Another portion of the cloth is placed in a solution of chloride of lime.
 - a. Colour unaltered Prussian blue.
 - b. Sample discoloured or turned yellowish Blues 3 or 4.
- III. In order to distinguish between these two blues we put a third swatch into a solution of caustic soda.
 - a. Sample discharged or altered Aniline.
 - b. Sample unchanged Indigo.

We may satisfy ourselves of the correctness of our results by the application of the following corroborative tests:—

The Blue of Logwood is reddened by acids and restored by caustic soda. The cloth when burnt leaves white or grey ash; the whiteness being due to the alumina of the alum used as a mordant, and the grey tint caused by the oxide of copper contained in the blue vitriol used with the wood. If copper is present the edge of the flame appears green during combustion.

Prussian Blue being a cyanide of iron leaves on combustion a red ash, oxide of iron, more abundant in proportion as the blue is deeper.

Indigo Blues contain no mineral matter, and leave no ash except that of the cloth. They may be either vat-colours, China blues, pencil blues, or extract of indigo. These are distinguished as follows:—

- I. Indigo, Vat.—A piece of clean white silk rubbed on the cloth becomes smeared. Sulphuric and muriatic acids, and carbonates of soda and potash, produce no change. Strong nitric acid destroys the blue, leaving a clear yellow, if no other colouring matter is present. Chlorine destroys the colour.
- 2. Indigo, China Blue.—Behaves like a vat-blue. If the colour is destroyed with chlorine, the cloth is not dyed on dipping in logwood liquor.
- 3. Indigo, Pencil Blue.—Behaves like the two former, but if dipped in logwood liquor after the colour has been destroyed with chlorine it is dyed red.
- 4. Extract of Indigo.—Unlike a vat-blue, it does not soil white silk on friction. Strong alkalies dissolve the colour, forming a blue solution. Nitric acid destroys it more rapidly than a vat-blue.

Aniline Blues when burnt leave merely the ash of the fabric. On steeping a swatch of the cloth in alcohol we obtain a beautiful blue liquid, not reddened by citric acid. The liquid obtained from a logwood blue turns red at once if mixed with an acid. Dilute acids and solutions of the carbonates of soda and potash produce no change. Concentrated acids turn the blue to a green, but washing in abundance of water restores the blue, in a somewhat fainter shade. Caustic soda turns the blue to a reddish-brown.

Prussian Blues.—Dilute acids produce no change. Concentrated nitric acid alters the shade to a green, which washing does not re-convert into blue. Solutions of alkalies, both caustic and carbonated, give a rust-colour (oxide of iron), different from the red shade which caustic soda gives on aniline blues,

and incapable of re-conversion into blue by washing in water.

Mixed Blues.—Vat-blue, in order to economise indigo, is sometimes "topped," and in other cases "grounded," with the red woods,—especially camwood and sanders,—with cudbear, and even with yellows, as fustic. In this case sulphuric and muriatic acids should be applied, at first dilute and afterwards concentrated, noting if the liquid is turned red or yellow. In the former case wood or weed colours are present. If a vat-blue, grounded with any other colour, is discharged with concentrated nitric acid, the colour remaining is not the clear yellow which unmixed indigo gives under similar circumstances, but a brownish shade.

Ultramarine Blue (Pigment Styles).—The swatch is steeped for a time in a mixture of ether and alcohol, to remove any resinous matter with which the colour may have been fixed, and then moistened with hydrochloric acid. The colour disappears, with the smell of putrid eggs.

C. YELLOWS.

The yellows on whose nature we are able to pronounce are:

- I. Iron buff.
- 2. Picric acid.
- 3. Turmeric.
- 4. Fustic.
- 5. Weld.
- 6. Persian beries.
- 7. Bark (quercitron).
- 8. Chrome yellows and oranges.
- 9. Annatto.

I. In order to distinguish between these colours, we begin by ascertaining the presence or absence of iron-yellow and of picric acid. To effect this, two swatches of the cloth are cut off, and the one is steeped in a luke-warm and slightly acid solution of yellow prussiate of potash, and the second in a hot solution of cyanide of potassium. If the prussiate gives a blue colour we may be certain that the sample is an iron-buff. If the cyanide gives a red colouration picric acid is present. Picric acid is extracted by alkalies and albumen. Acids produce no change.

II. If neither of these results appears iron and picric acid are both pronounced absent. We then take a fresh swatch and put it in a boiling solution of 1 part of soap in 200 of water. The following reactions may then take place:—

- b. The cloth is nearly decolourised Fustic.
- c. The soap has little or no action. In this latter case we may have weld, berries, or bark.

To distinguish these three colours, we take a fresh swatch and submit it to a bath of very dilute boiling sulphuric acid. If the colour fades it is weld; if it does not change it is berries or bark. We then take another swatch and soak it in a solution of tin crystals. If the colour changes to orange it is berry-yellow. If scarcely affected it is bark or flavin.

If we suspect a bottom of annatto we soak a swatch in concentrated sulphuric acid. The colour changes suddenly to greenish blue. Annatto is the only tinctorial body presenting this reaction. Bark, berries, fustic, turmeric, and weld are all bleached by chlorine. Annatto resists this reagent. Fustet (young fustic) is rarely met with, except in wool-dyeing.

Chrome Yellows and Oranges.—Sulphuretted hydrogen or alkaline sulphides blacken them. They are destroyed by caustic soda.

Annatto.—Chlorine and bleaching-liquor have little action. Concentrated sulphuric acid turns it a bluish-green. Nitric acid discharges.

D. REDS.

The red dyes that may present themselves are the following:-

- 1. Cochineal.
- 2. Brazil wood, &c.
- 3. Madder and garancin.
- 4. Safflower and carthamin.
- 5. Aniline-red.
- 6. Murexide.
- 7. Corallin.
- 8. Weed-colours, orchil, cudbear, &c.

We begin by ascertaining the presence or absence of madder-red. We place in four glasses or capsules the following reagents:—Boiling soap-lyes, caustic ammonia, citric acid (or lemon juice), a mixture of equal parts of tin crystals, hydrochloric acid, and water. In each of these a swatch is plunged. If all four remain unattacked we have madder-red. If there is a change we infer its absence and the presence of one of the other reds.

Complete decolouration by soap-lyes indicates safflower. In this case the colour reappears with its original shade on washing in pure water and brightening with citric acid. If on washing with water and brightening the colour reappears fainter, we have aniline red. If the washing and brightening change the red to an orange or yellow, we have cochineal or Brazil-wood. We may distinguish between these two colours as follows:—A swatch of the original fabric, steeped in sulphuric acid, is turned a cherry-red if it be Brazil-wood, and a yellowish orange if cochineal.

Murexide.—It is discharged by citric acid and by boiling soap-lye.

Corallin.—If a swatch is digested in hot alcohol the colour is extracted. The addition of ammonia then brightens the liquid.

Weed-Colours, Orchil, Cudbear, &c.—Destroyed by solution of tin crystals.

E. GREENS.

The greens most commonly met with in dyed goods are of three kinds:-

r. Greens obtained with a mixture of yellow and blue.

2. Aniline (aldehyd) green.

3. Iodine green.

Lao-kao, chlorophyl, &c., are rarely met with. The greens made up of vellow and blue are .-

r. Indigo and pieric acid.

- 2. Indigo and vegetable yellows.
- 3. Prussian blue and picric acid.
- 4. Prussian blue and vegetable yellows.
- 5. Aniline blue and vegetable yellows.

6. Aniline blue and picric acid.

In these mixed greens the blues form the bottom and, excepting aniline blue, are insoluble in alcohol. All the yellows given are soluble in alcohol. Hence a green, soluble in alcohol with a green colour, must be a mixture of aniline blue and yellow.

Into a small flask is poured some alcohol at 95 per cent, into which a swatch of the cloth is immersed. The alcohol is raised to and maintained at the boiling-point for a few minutes on the water-bath. Two results may

- I. The alcohol becomes yellow, and the tissue turns gradually more blue.
- 2. The alcohol becomes green, whilst the cloth grows paler, but without altering its tone.

In the former case the bottom is indigo or Prussian blue. When the swatch has given up all its yellow colour to the alcohol, it is taken out, washed in pure water, and placed in a glass with a solution of chloride of lime. If the bottom is indigo, the colour will be attacked, but if Prussian blue, it will remain unchanged. The alcoholic liquid remaining in the flask may contain several colouring matters. It is divided into portions, which are then tested according to the instructions given for yellows.

In the second case we have aldehyd or iodine green, or aniline blue along with a yellow. In order to distinguish between these colours, we boil a swatch in dilute hydrochloric acid. The cloth becomes:-

- a. Rose or lilac Iodine green.
- b. Blue, the yellow being discharged Aniline blue and a yellow.
- c. Discharged, or yellowish Aldehyd green. If it be found that the green is a mixture of aniline blue and a yellow, the

nature of the latter may be determined as above directed.

A swatch may be placed in a solution of carbonate of soda, noting whether a blue colour is dissolved out. If so, the blue portion of the green is extract of indigo. If the swatch is turned a rusty colour by alkalies, the blue is a Prussian. This is most to be expected on cotton goods. If the green is blackened by sulphuretted hydrogen, and if a blue remains on carefully washing with a dilute acid, chromate of lead is one of the ingredients. In this case, for corroboration, burn a swatch to ashes in a light porcelain-not platinumcapsule, and extract the ash with dilute nitric acid. If chromate of potash gives a yellow precipitate in the filtered liquid, chrome-yellow was originally present.

If the green is a chrome-green, such as Guignet's, oxide of chrome will remain in the ash, which will have a dull green colour.

If the green is arsenical, such as Scheele's green, a piece of the cloth, on burning, gives a green tinge to the flame. The ash is extracted with nitric or hydrochloric acid. The clear solution is freed from excess of acid by evaporation at a gentle heat, diluted with a little water, and mixed with ammonia in excess. A blue colour will appear from the copper present in the arsenical greens.

On woollen and worsted goods, if soda dissolves off extract of indigo, the yellow portion will probably be fustic. If the blue is a Prussian or royal, the yellow will generally be bark or flavin.

F. VIOLET.

The violets here indicated are:-

- I. Common aniline violet.
- 2. Iodine (Hofmann) violet.
- 3. Madder purple.
- 4. Alkanet violet.
- 5. Orchil violet.
- 6. Logwood violet.
- 7. Cochineal purple.

We first steep a swatch in solution of chloride of lime. If it resist it is alkanet violet. If there is a change of colour we have one of the six others.

A second swatch is then steeped in lime-juice. If the violet be not heightened in tone we have one of the two aniline violets. If it becomes red, or even yellow, we may have madder, orchil, cochineal, or logwood. To distinguish these a swatch is steeped in chloride of lime, then washed in water, and placed in an acid solution of yellow prussiate of potash. As madder and cochineal purples have oxide of iron for their mordant, which remains attached to the fibre, Prussian blue is formed in case of these two colours. If there is no blue colouration, we have orchil or logwood. It remains then to distinguish between—

- I. Madder purple and cochineal purple.
- 2. Orchil violet and logwood purple.
- 3. Common aniline violet and Hofmann violet.

A fresh swatch of the cloth is steeped in chloride of lime. It is turned a Nankeen yellow if dyed with madder, and is completely discharged if dyed with cochineal.

A swatch steeped in milk of lime becomes greyish, and, finally, colourless if dyed with logwood; but changes to a violet-blue if dyed with orchil.

A swatch steeped in hydrochloric acid diluted with three times its measure of water becomes blue-violet, and after washing with water a little redder, in case of common aniline violet. In case of iodine (Hofmann's) violet, the fabric becomes blue, greenish, and after washing with water a clear lilac, or pearl-grey, according to the original depth of shade.

A red ash (iron mordant) indicates madder or cochineal. A white ash (alum mordant) indicates logwood. Absence of ash shows the aniline violets.

A peculiar pigment violet is produced by a mixture of ultramarine and vermillion. If this is treated with dilute acid the blue is destroyed, while the red

of the vermillion remains. Subsequent treatment with an alkali does not affect the red or restore the original shade.

In all these directions it must be understood that madder comprehends garancin and alizarin, natural or artificial. Cochineal must, in like manner, be taken to include lac.

The nature of the fibre often gives a clue to the colour, which should not be overlooked. Thus among yellows, picric acid is not to be expected upon cotton, nor is iron-buff often found upon wool. Reds upon cotton are rarely cochineal,—usually madder, or the woods. Upon woollen or worsted, cochineal or magenta is more probable. Upon cotton, aniline blues are less likely than upon wool and silk.

Behaviour of Colours on Different Fibres with Reagents. I. Aniline Colours.

						D	E7	ECT	10	N	0	F	D	YES							669
Ammonic Cuprate.	Slight discharge.	Violet.	Violet.	Dark blue.		Grad. discharge.	Violet.	Light yellow.	Yellowish-rose.	Greenish.	Light violet.	Greenish-yellow.	Yellow.	Reddish-yellow.	Yellowish-rose.	Discharge.	Blue.	Violet.	Rose.	Violet.	Dark green.
Soda.	Quick discharge.	Gradual discharge.	Slight discharge.	Slight discharge.		Instant discharge. Grad. discharge.	Violet.	Light violet to yellow.	Yellowish-rose.	Light yellow-green. Lightyellow-green. Greenish.	Very light yellow. Light violet.	Straw-yellow.	Light yellow.	Discharge to light yellow.	Yellowish-rose.	Light violet.	Slow discharge.	Pale rose.	Discharge.	Green, then dirty yellow.	Yellow-green.
Dilute Sulphuric.	Light blue.	Faint greenish.	Discharge.	Discharge.		Light green.	Pale light green.	Discharge.	Light yellow.	Light yellow-green	Discharge.	Discharge.	Light yellow.	Dirty rose.	Light yellow.	Discharge.	Slow discharge. Slow discharge.	Pale blue.	Discharge.	Green, then dirty yellow.	Yellow-green.
Acid Chromic.	Green.	Light green.	Light greenish. Discharge.	Light green.		Light green.	Violet.	Light violet.	Light yellow.	Light green.	. Light yellow. Discharge.	Dirty light brown. Straw-yellow. Discharge.	Straw-yellow. Light yellow.	Dirty light brown, Dirty rose.	Light red-orange. Light yellow. Light yellow.	Light violet. Discharge.	Slow discharge.	I scharge.	ischarge.	Discharge.	Very light green.
 Iodine.	Green.	Dark yellow.	Yellow.	Green, then	orange.	Gold-yellow.	Yellow.	Orange.	Dirty green.	Orange.	Orange-yellow.	Dirty light brow	. Orange.	Dirty light brow	Light red-orang	Orange.	Yellow.	Yellow.	Orange.	Light violet.	Light green.
Microscop. Colour.	Blue & blue-black. Green.	Violet.	Very light violet.	Pale blue.		Green.	Light red.	Violet.	Light blue.	Light green.	Yellow.	Straw-colour.	Yellow and brown.	Vinous red.	Light rose.	n.Violet.red.	Blue-black.	Violet.	Red.	Violet.	Light green.
Colour.	Black.	Dark violet.	Light violet.	Blue.		Green.	Red.	Dahlia.	Rich blue.	Iodine-green.	Aniline-yellow.	Iodine-orange.	Bismark-brown.	Maroon.	Magdala-red.	Diamond-fuchsin. Violet red.	Black.	Violet.	Red.	. Dahlia.	Green.
	Silk.							Cotton.									Linen.			China Grass. Dahlia.	

II. Cochineal Colour.

	Ammonic Cuprate. Red-violet.		Violet.		Dirty orange.		Light violet.	Deep violet.
	Soda. Light rose.		Violet.		Discharge.		Discharge.	Violet.
	Dilute Sulphuric. Rose.		Light rose.		Light rose.		Green.	Dirty red.
a. Natural.	Acid Chromic. Rose.	b. Ammoniacal Paste.	Light red-orange. Light rose.	III. Safflower.	Red.	IV. Orchil.	Violet.	Red.
	Iodine. Red-orange.	b. A.	Light red-oran	II	Red-brown.	I	Yellow.	Red.
	Microscop. Colour. Red.		Light red.		Rose.		Violet.	Ked-brown.
	Colour. Red.		Red.		Rose.		nt Violet.	Red-brown.
	Wool.		Wool.		Cotton.		Silk, without Violet.	Wool.

V. Madder Colours.

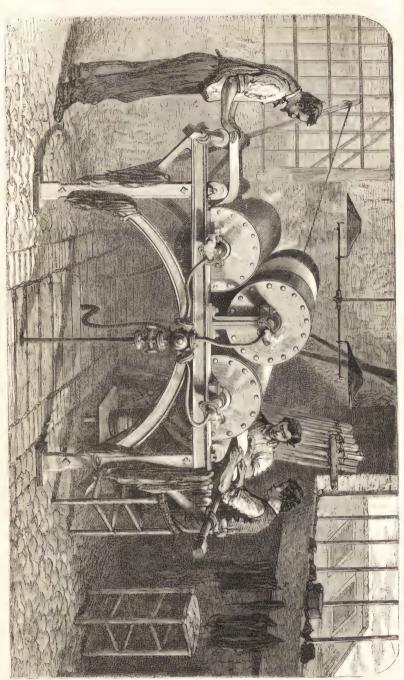
a. Alizarin, Natural and Artificial.

				DE	ILCII	UIV C	11,	DI	1213	•				C	7 ^
	Amn.onic Cuprate.	Violet.	Violet. Red. Red.	•	Red-violet.	Deep violet-red.		Red-violet.		Violet.	Slight dis- charge.	Light rose.	Light rose. Rose, slow dis-	0	Red.
	Soda,	Violet.	Rose. Rose. Yellow-rose.		Rose.	Violet-rose.		Rose.		e.Violet.	Yellowish discharg- Slight discharge, ing.	t Rose.	Pale rose. Red.		Red.
,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	Dijute Sulphuric.	Pale yellow dis- charge.	Orange. Discharge. Yeliow.		Light red.	Yellow-rose.		Rose.	VS.	Light yellow. Yellowish discharge. Violet.	Yellowish discharging.	Yellowish red faint Rose. discharge.	Discharge. Discharge.		Rose.
the distinctions are with the contract of	Acid Chromic.	Discharge.	Orange-rose. Discharge. Orange.	b. Purpurin.	Red-orange.	Deep orange. Yellow-rose.	c. Garancin.	Light red.	d. Common Madder Colours.	Light yellow.	Yellow.	Slightly dis- charging.	Yellowish. Rose.	e. Turkey-Red.	Rose.
18. 126121111111	Iodine.	Yellow.	Rose. Red-brown. Rose.	p	Deep orange.	Orange.	0	Red-orange.	d. Comma	Light yellow.	Yellow.	Red-yellow.	Yellowish. Red.	o	Orange.
	Microscop, Colour.	Light violet.	Light claret. Rose. Red.		Deep red.	Red.		Red.		Violet.	Light violet.	Red-violet.	Light rose. Claret.		Rose and red.
	Colour.	Violet.	Red-brown. Light red. Deep red.		Deep red.	Wool with Red-orange. Tin Mordant.		Red.		Chocolate.	Violet.	Red-brown.	Rose. Red.		Red.
		Cotton and Violet.			Wool with Deep red. Alum Mor-dant.	Wool with Tin Mor-		Cotton.		Cotton and	Linen.				Cotton.

VI. Fustic, Flavin, and Quercitron Extract.

	Armonic Cuprate. Light yellow. Dirty yellow.		Yellow.		Very slowly blue.			Dirty green blue.		Blue.		Dirty brown. Green-blue. Dirty blue.
	Soda. Light yellow. Yellow.		Orange-yellow.		Yellow.			Blue.		Discharge.		Dirty violet. Light yellow. Dirty yellow.
ron Extract.	Dilute Sulphuric. Light yellow. Light yellow.		v. Light yellow.	ow.	Yellow.			Blue.	tic Acid).	Dark blue.		Green, then red. Blue. Greenish blue.
n, and Querciti	Acid Chromic. Light yellow. Yellow.	VII. Persian Berries.	Yellow-green to Intenseyellow. Light yellow. violet.	VIII. Naphthalin Yellow.	Yellow.	IX Indian.	a. Vat Blues.	Green-blue.	igo (Sulphindigo	Green-blue.	X. Silk Black.	. Yellow. Blue-green. Green.
VI. Fustic, Flavin, and Quercitron Extract.	Iodine. Light yellow. Dirty yellow.	VII. F	Yellow-green to violet.	VIII. N	Deep yellow. Yellow.	1	a.	Green and dirty Green-blue, yellow.	b. Extract of Indigo (Sulphindigotic Acid).	Yellow-green.	×	Greenish yellow. Yellow. Light green. Blue-gre Blue-green. Green.
V.	Microscop. Colour. Light yellow. Dark yellow.		Light Yellow.		Yellow.			Light blue.	9	Light blue.		Blue-brown. Deep blue. Blue.
	Colour. Yellow. Brown.		Yellow.		Yellow.			Blue.		Blue.		Black. Black. Black.
	Cotton and Yellow. Linen. Brown.		Cotton and Yellow. Linen.		Wool.			Cotton.		Wool.		Silk.





FINISHING MACHINE.

APPENDIX.

1. Preparation of Picric Acid.—Guinon arranges in a sand-bath two series of flasks, each containing an equal weight of nitric acid of sp. gr. 1'3. Crude carbolic acid is allowed to flow drop by drop into each from a vessel placed above, through glass tubes, no external heat being applied. All the flasks communicate by means of glass tubes with a large stoneware vessel. which receives the acid fumes given off; part of them are condensed there, and the rest escape through the chimney. When the falling drops of carbolic acid undergo no further change, the supply is cut off, and a gentle heat is applied to the sand-bath, to effect the transformation of the resinous mass still floating in the flasks. The contents are finally poured into capsules where the picric acid is deposited, on cooling, partly in coherent clots, and partly in fine crystals. It is placed in a funnel, the throat of which is loosely filled with fragments of quartz or of bricks free from lime. The nitric acid gradually drains away, whilst the picric remains. It is still contaminated with a little resinous matter, to remove which it is dissolved in boiling water containing Take of sulphuric acid, in which the impurities remain insoluble. Perra prepares picric acid as follows: -- 600 parts by weight of nitric acid, of sp. gr. 1.3. are placed in a flask, and 100 parts of carbolic acid are gradually added. The nitric acid volatilised during the reaction is condensed by means of a cohobator, and allowed to flow back upon the carbolic acid. The yield thus obtained varies from 90 to 110 per cent of the carbolic acid employed.

Carey Lea prepares picric acid from Australian "Yellow Gum," the resin of Xanthorrhwa hastilis, as follows:—150 grms. of the resin, powdered and placed in a capsule containing 2 or 3 litres, are moistened with 300 grms. of nitric acid, of sp. gr. 1'42. As soon as the action begins 750 grms. of boiling water, which should be ready at hand, are added. Heat is applied, when the mass swells up and threatens to run over, which must be prevented by the addition of small quantities of cold water and by a judicious regulation of the temperature. When the volume of the liquid has diminished one-half, 150 more grms. of nitric acid are added, and the heating is continued till the liquid is reduced to its former bulk. From 120 to 200 parts of nitric acid are still required to complete the operation. The liquid is then evaporated down to the bulk of 120 to 150 c.c. On cooling the residue solidifies. The yield is

from 25 to 50 per cent of the yellow gum employed.

2. Isopurpuric Acid.—The best results are obtained with an isopurpurate of aniline. To obtain this salt, which is formed in the dye-beck, 100 parts isopurpurate of potash are mixed with 42 parts hydrochlorate of aniline.

Wool which has previously been boiled for two hours in the ordinary manner with 4 parts of alum and 1 cream of tartar takes rapidly a chestnut-brown colour. Silk mordanted with alum (to which one-tenth of its weight of soda crystals have been added) dyes up a rose with a violet tinge in the isopurpurates of potash or ammonia, but a deep garnet brown with the isopurpurates of baryta or aniline.

3. Rosolic Acid.—Jourdin heats phenate of soda with peroxide of mercury to a little above 150° C. for ten minutes, and obtains thus a rich red solution

of the rosolate of soda.

Kolbe mixes in a tubulated retort 1 part of oxalic acid, 1½ of carbolic acid, and 2 of sulphuric acid, and heats to 140° to 150° C. for 4 to 5 hours. The red-brown residue, as soon as it begins to swell up, is thrown into water and boiled, adding fresh portions of water till the odour of carbolic acid disappears. The deep-brown paste which remains undissolved, dissolves in ammonia with a magnificent purple colour.

- 4. Fol's Yellow.—This colour, derived from carbolic acid, is of an acid nature, and forms red compounds with bases. To prepare it heat for twelve hours, at 100° C. in an open cast-iron boiler, 5 parts of carbolic acid and 3 parts of arsenic acid, dried and finely powdered. The colouration appears at the end of two hours, and increases gradually in intensity as the matter thickens and gives off steam. After 12 hours the temperature is raised to 125° C., and kept at that heat for 6 hours. When the mass ceases to swell up 10 parts of acetic acid at 7° B. are added. The mass is dissolved in abundance of water, the solution is filtered through calico, and mixed with salt in excess, which precipitates the colouring matter in flocks. It is purified by combining with baryta and decomposing the barytic salt with sulphuric acid. The pure product separates out in the form of reddish-brown lamellæ. It dissolves easily in cold and hot water, ether, alcohol, and wood-spirit. In presence of caustic or carbonated lime or baryta it dyes wool and silk all shades of red. These colours are not affected by soap. If used alone it gives varied shades of yellow. It is frequently employed along with rosolic acid and other colours to produce browns.
- 5. Campo-Bello Yellow is prepared by a secret process by Schrader and Berend, of Schönefeld, Leipzig. It is a derivative of carbolic acid, and is advantageously used in wool-dyeing. It produces all shades of yellow, and resists solutions of carbonate of soda at 20° B. For use it is dissolved in boiling water and filtered. The solution is boiled, and the wool plunged for half an hour in the boiling liquid; 300 grms. of alum may be added for each 5 kilos. of wool. Campo-bello yellow mixed with magenta, indigo, &c., yields a variety of useful colours.

6. Phenicienne.—The nitro-sulphuric acid employed in preparing this colour consists of 2 volumes of common oil of vitriol and 1 volume of nitric acid, at sp. gr. 1'35.

7. Chloride of Benzyl.—Lauth and Grimaux have obtained a fime violet by the direct action of chloride of benzyl upon rosaniline, and when Hofmann's "Violet R" is used in place of rosaniline a violet is formed of a decided blue shade. For the preparation of chloride of benzyl an apparatus

is employed which can be used at will either for cohobation or distillation. Toluen is introduced into this apparatus and quickly brought to a boil, and a current of chlorine is brought in contact with its vapours, which are directed into the cohobator, where the toluen and the chloride of benzyl formed are condensed and fall back. When a thermometer immersed in the boiling toluen marks 140° to 150° C., the current of chlorine is shut off and distillation begins. All that passes over below 170° C. is collected separately, and is again treated with chlorine. What distils between 170° and 180° is submitted to a new rectification. Finally, what goes over between 174° and 176° C. is nearly pure chloride of benzyl.

8. Diphenylamine yields a magnificent blue colour with concentrated nitric acid, methyl-diphenylamine, which is obtained by treating diphenylamine by iodide of methyl at temperatures above 100° C. It yields blue or violet compounds with arsenic acid, the metallic nitrates, chlorides, iodides, bromides, iodine, chlorate of potash, sesquichloride of carbon, chloral, &c.

g. Cerise.—The trade name of a colour sold by the firms of Geigy, of Basle, and Knosp, of Stuttgardt. It is prepared from magenta residues, and dyes shades more inclining to a scarlet. After the crude magenta has been boiled in water and the pure magenta precipitated with common salt, carbonate of soda is added to the remaining liquid, and the precipitate thus obtained is collected and dried. It is probably a mixture of rosaniline with chrysaniline and chrysotoluidine.

ro. Coupier's Aniline Reds.—Coupier dispenses with arsenic, and obtains reds—(1) with pure or nearly pure aniline and nitro-toluen; (2) with ordinary commercial aniline and common nitro-benzin; (3) with nitro-toluen and toluidine or with nitro-xylen and xylidine. In each case he adds perchloride of iron and hydrochloric acid. The two former mixtures yield reds identical with common magenta; the third gives a product which Coupier names roso-toluidine, toluidine-red, or xylidine-red. The ingredients to be used for the last-mentioned colour are:—

The method of conducting the operation on the large scale is as follows:—Any of the above mixtures is placed in an enamelled cast-iron vessel, and heated gradually to 200° C. The progress of the reaction is judged by the indications of a thermometer plunged in the mass, by the nature of the vapours given off, and by the appearance of the mixture, of which a specimen is taken from time to time. The product, on cooling, becomes a solid, brittle mass, like raw magenta-melt. It is powdered, boiled in water, and the colouring matter is thrown down by means of carbonate of soda, and purified in the ordinary manner.

xII. Hofmann's Xylidin Red is prepared by heating a mixture of pure xylidin and pure aniline with an oxidising agent. It is a splendid crimson-red colour, producing shades very similar to those yielded by magenta. It is evidently distinct from Coupier's xylidin-red.

12. Ulrich's Scarlet.—Mix 4 parts by weight of acetate of rosaniline and 3 parts nitrate of lead dissolved in the smallest possible quantity of boiling water; the mixture is boiled and evaporated to dryness. The dry mass is heated to 150° to 200° C., until it suddenly becomes violet. When cool it is again boiled for some time in water slightly acidulated with sulphuric acid. The acid solution is neutralised with an alkali and filtered whilst boiling. From the filtrate the colouring matter is thrown down by means of common salt. The precipitate is collected on a filter and dried.

This scarlet, on ethylation or methylation, furnishes a rose-red colouring matter. For this purpose it is dissolved in alcohol, the solution mixed with iodide of ethyl (or methyl), and heated for some time in an autoclave. From the product the new colouring matter is extracted in the same manner as

Hofmann's violet.

13. Hofmann Violet, RRR.—The accompanying pattern, kindly furnished by Messrs. Brooke, Simpson, and Spiller, shows the reddest shade of the Hofmann violets, the manufacture of which has been described upon p. 192. The colour is perfectly soluble in hot water, and upon animal fibre requires no mordant. In dyeing woollens, the goods are entered at 120° F., and dyed slowly up to the boiling-point. Care must be taken not to overload the beck with colour.

14. Dorothea Violet.—H. Lewinstein produces this colour, which approximates to Hofmann's violet, by mixing 50 parts of alcohol at 90 per cent, 35 parts of rosaniline, and 7 parts of nitric ether, and heating the mixture to 100° C. for two or three hours.

15. Wanklyn's Violet.—The inventor prepares first the iodide of pseudopropyl by acting upon glycerin with hydriodic acid. This body is then mixed with an equal weight of rosaniline, and with the addition of alcohol is heated to 100° C. in closed vessels. The resulting mass is treated with caustic sodalye, and the violet dye is thus obtained in a state sufficiently pure for use.

16. Paris Violet (Poirrier's Violet).—The patentees take—(1) 50 or 80 parts by weight of methylic alcohol and 100 parts of hydrochlorate of aniline; (2) 100 parts of commercial aniline, 160 parts of sal-ammoniac, and 50 or 80 parts of methylic alcohol. These mixtures are heated for three or four hours in an enamelled Papin's digester to 250° or 300° C. The latter mixture attacks the iron less. Hydriodate or hydrobromate of aniline may be used instead of the hydrochlorate, and require a lower temperature. The product of the reaction is repeatedly washed with a lye of caustic soda, which decomposes the salts of methylaniline or ethylaniline formed. The oil thus separated is rectified, and is then sufficiently pure. The product obtained is mixed with 5 or 6 parts of anhydrous chloride of tin with brisk agitation. The mixture is heated to 100° C., and at the expiration of some hours it becomes hard and solid. When the reaction is at an end the mass is allowed to cool. It is freed from all foreign matters by boiling the mass with caustic soda and washing it therewith, when the base of the colouring matter remains with a deep shade. The colour is then regenerated by the addition of any acid. Instead of the process with chloride of tin we may take:-

Sulphate of methylaniline 100
Chlorate of potash, powdered 100 to 150
Water 100 to 150

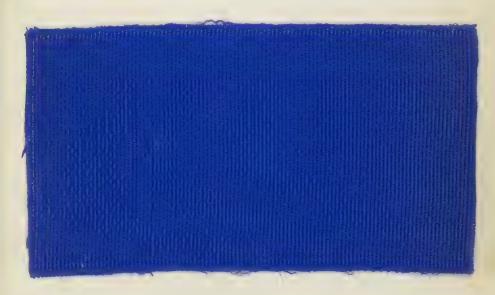


HOFMANN VIOLET, RRR.

and heat for several hours to 160° C. The dye produced is very soluble in water even in the cold.

17. Lauth's Violet.—According to the last improvement the patentee heats methylaniline to 120° with half its weight of hydrochloric acid till the colouring matter is formed; or to 100° C. with half of its weight of nitrate of copper; or he heats to 100° C. I part of acetate of methylaniline with ½ part oxide of mercury. The longer the mixture is heated the more blue are the shades produced.

18. Spiller's Purple.—This colour is a violet of a very blue shade, manufactured by the distinguished firm of Brooke, Simpson, and Spiller, to whose kindness we are indebted for the accompanying specimen.



SPILLER'S PURPLE.

19. Methyl-diphenylamine Violet.—Place upon copper plates arranged in a stove heated by steam—

Hydrochlorate of methyl-benzyl-p.	henylan	nine	 3 kilos.
Sulphate of copper			 I kilo.
Chlorate of potash			 0'2 ,,
Siliceous sand			 20 kilos.
Hydrochlorate of essence of tereb	enthin		 2

The stove must be so arranged as to permit of a free circulation of air. An excess of moisture is kept up by the injection of a little steam, and the mixture is frequently stirred. The temperature is maintained at 45° to 70° C. The operation is considered at an end when nothing more of an oily nature is perceived. The product is then repeatedly extracted with boiling water, which takes up the soluble metallic salts. In order to dissolve the colouring matter mixed with the sand either alcohol or strong hydrochloric acid may be used. When the sand is exhausted all the coloured solutions are mixed and distilled if alcohol has been used, or diluted with water and precipitated with common salt if hydrochloric acid has been employed. The colour thus obtained is transmuted into a base by means of soda or potash. The base is washed with water and taken up with acetic or hydrochloric acid. These salts are very soluble and dye blue-violets

Others of the mixed tertiary monamines, as methyl-diphenylamine, benzyl-diphenylamine, benzyl-phenyl-toluylamine, and benzyl-ditoluylamine yield similar colours.

20. Paris Green.—Poirrier, Bardy, and Lauth prepare this new green colour by acting with an oxidiser—such as bromine, iodine, chlorine, weak nitric acid, nitrates of mercury copper and other metals, and solution of chloride of iodine in ten times its weight of water—upon benzyl- or dibenzyl-aniline, tolyl- or ditolyl-aniline, benzyl- or dibenzyl-toluidine, tolyl- or ditolyl-toluidine, and their mixtures.

21. Methylaniline Green.—This colour, which is generally replacing iodine green, is prepared by causing nitrate of methyl to react upon Poirrier's violet (methylaniline violet). The separation of the violet and green colouring matters is effected by the addition of a solution of chloride of zinc and gradual saturation with carbonate of soda. A zinc-violet lake is thrown down at first. When all the violet is precipitated and filtered off, the filtrate is concentrated and allowed to cool, when a double chloride of zinc and aniline green crystallises out.

22. French Yellow; Chryseic Acid (Nitro-xynaphthalic Acid of Dusart and Gelis).—If 100 parts of nitro-naphthalin are intimately mixed with 250 parts of dry hydrate of lime, and the mixture moistened with 75 parts of hydrate of potash dissolved in as little water as possible, and the whole heated for ten to twelve hours to the temperature of 150° C. in an oilbath with free excess of air, or preferably in a current of oxygen, the mixture becomes oxidised and assumes gradually a deep yellowish-red colour. On treating the mass with hot water and filtering the liquid, we obtain a yellow solution of the nitro-xynaphthalate of potash, and after sufficiently concentrating the liquid, the nitro-xynaphthalic acid may be precipitated by the addition of any strong acid, in the form of fine yellow flocks, soluble in hot water, alcohol, wood-spirit, and acetic acid. It dyes silk and wool a full golden yellow.

23. Carminaphtha.—If chromic acid, or a mixture of chromate of potash and sulphuric acid is allowed to act upon naphthalin, a fine red colouring matter is frequently formed, under circumstances not yet fully determined. It is a weak acid, almost insoluble in water, soluble in acetic acid and alcohol. With alkalies it forms orange compounds soluble in water, and it dyes silk and wool an orange or a red-violet without the aid of mordants.

24. Chloroxy-naphthalic Acid.—Naphthalin treated in the cold with the chlorate of potash and hydrochloric acid is transformed into a mixture of bichloride of naphthalin, bichloride of chloro-naphthalin, and certain secondary oily products, which are eliminated by pressure. The residue is heated in a water-bath and oxidised with nitric acid. It is needful to operate cautiously to avoid the formation of large quantities of phthalic acid, and that the bulk of the chloride of chloro-naphthalin may be converted into bichlorated naphtho-quinon, whilst the bichloride of naphthalin forms phthalic and oxalic acids. These acids are removed by boiling water, and the former is subsequently converted into benzoic acid.

The bichloride of naphtho-quinon, which is insoluble in water, is dissolved in boiling potash-lye; the deep-coloured solution is filtered and supersaturated with a mineral acid, when impure chloroxy-naphthalic acid is thrown down. This is re-dissolved in soda-lye and exactly neutralised. To the neutral solution a little alum is added, which precipitates a brown impurity. The liquid is filtered afresh and mixed with a mineral acid, when the pure chloroxy-naphthalic acid falls as a yellow crystalline powder.

It is soluble in boiling water, alcohol, ether, and benzine. It dissolves without decomposition in concentrated sulphuric acid, from which it is re-precipitated on the addition of water. It dyes wool an intense red without the aid of a mordant. If chloroxy-naphthalic acid in an alkaline solution is reduced by means of tin powder, and the solution is boiled for fifteen or twenty minutes, a yellow liquid is obtained, which when mixed with ammonia and left to itself, turns green after some time. If it is neutralised with a mineral acid a brown flocculent body is precipitated, which when washed and dried appears as a green powder with a metallic reflection. It is monochlorated trioxy-naphthalin. It dissolves in boiling aniline with a red, and in sulphuric acid with a green colour. From the latter solution it is thrown down by water with a violet colour. It dissolves in alcohol with a violet colour, which turns blue on dilution with water. Mono-chlorated trioxy-naphthalin dyes wool and silk a violet, and may be fixed upon cotton with the aid of albumen.

25. Ballo's Violet.—Magenta, in the form of acetate of rosaniline, heated with naphthylamin or with bromated naphthalin, gives a fine violet.

26. Naphthoic Blue.—The attempts made by Girard, and by Mylius, of Basle, to replace benzoic acid with naphthoic acid in the conversion of magenta into rosaniline blue, have shown that the latter, which is cheaper, gives a blue at least as bright and beautiful as that produced by means of benzoic acid.

27. - Aniline Grey (Castelhaz).-

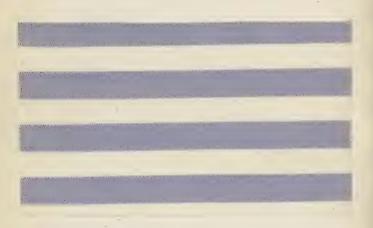
Aniline grey (Gris Castelhaz, p. 210) I gallon.

"Reduction paste," see below 4 gallons.

Boil till dissolved.

When printed, the pieces are steamed for thirty minutes.

28. Naphthols, or Naphthylic Alcohols.—If the alkaline salts of sulphonaphthalic acid are fused with the hydrate of soda we obtain the naphthols,



Aniline Grey (Castelfiaz).

which bear the same relation to naphthalin as does phenol to benzine. One part of dry sulphonaphthalate of soda is melted in an iron, copper, or silver capsule, with two parts of dry hydrate of soda; the mass is dissolved in boiling water, cooled, and the clear solution decanted, and mixed with hydrochloric acid. Sulphurous acid is given off, and naphthol is thrown down in a crystalline state. It is filtered, slightly washed, and re-crystallised from boiling water.

Naphthol α can be sublimed, and crystallises in brilliant white needles. It melts at 94° C., and dissolves readily in alcohol, ether, and benzine, and sparingly in water. The aqueous solution takes an intense violet colour if mixed with a solution of chloride of lime, and deposits brownish-red flocks if heated.

Naphthol β crystallises in brilliant lamellæ, and melts at 122° C. With chloride of lime it takes a yellowish colour, and the liquid, if heated, deposits yellow flocks. In solubility it agrees with the α variety. A chip of pine-wood steeped in the aqueous solution of the naphthols, mixed with hydrochloric acid, and then exposed to sunlight, takes a green colour, which afterwards passes into a brownish-red. The two naphthols, if treated in a dry state with concentrated sulphuric acid, yield sulphonaphtholic acids. If sulphonaphtholic acid α is mixed with nitric acid a red colouration appears, and binitronaphthol (Martius's yellow) separates.

Sulphonaphtholic acid β does not give this reaction, but naphthol β may be converted into binitronaphthol β by treating its alcoholic solution with nitric acid. The latter compound crystallises in brilliant yellow lamellæ, sparingly soluble in water, readily in alcohol, and very readily in ether and chloroform. Its solutions due wool and silk a full, beautiful yellow.

29. Anthracen-Orange.—If binitro-anthraquinon is treated with reducing agents, such as stannite of soda, sulphuret of antimony, or sulphuret of sodium, it is transformed into a colouring matter, the anthracen-orange of Bœttger. It is prepared as follows:—

The stannite of soda is obtained by mixing with a moderately concentrated soda-lye a clear saturated solution of the protochloride of tin, containing as little free acid as possible. It is poured in a slender stream into the lye, with constant stirring, until a slight turbidity begins to appear in the liquid. It is then left to settle, protected as far as possible from contact with the air, and the clear portion is decanted through a filter. With this the binitroanthraquinon—washed and still damp—is drenched. A beautiful and intensely green liquid is immediately formed, and if boiled without interruption anthracen-orange separates in abundance, after a short time, as flocculent powder, of a cinnabar-red. If this colour is moistened with water, dried, and submitted to sublimation in a porcelain crucible placed in a sand-bath, it fuses at 235° C., and from that point to 260° it sublimes in crystals of a garnet-red, with a green metallic reflection.

Its best solvents are acetic ether, aceton, chloroform, aldehyd, ether, alcohol, and wood-spirit. It is slightly soluble in bisulphide of carbon, but is insoluble in petroleum and naphtha. At ordinary temperatures it dissolves in sulphuric acid (full strength) without decomposition, even at a boiling heat, forming a brownish-yellow liquid, which, if largely diluted with water, deposits a flocculent mass of a fine red colour. It dissolves also without decomposition, at common temperatures, in nitric acid of specific gravity 1.2. But if heated for some time with a solution of mercuric nitrate it is transformed into a deep violet powder, which dissolves in ether with the same colour. If, instead of heating the original green liquid obtained on treating binitro-anthraquinon with stannite of soda, it is immediately poured into dilute sulphuric acid, a flocculent reddish-brown precipitate is formed, which if filtered, washed, and dried, and then dissolved in alcohol, leaves, after removal of the alcohol, a brown colouring matter, which dissolves in acetic ether with a deep purple-red colour.

If a solution of anthracen-orange in ether is treated with nitrous acid, a fine powder of a violet-brown is deposited, easily soluble not only in alcohol, but also in water, with a fine deep violet-red colour. If the dry powder is heated to about 68° C. it detonates.

If binitro-anthraquinon is boiled for a long time with aniline, the latter takes a deep red-brown colour, and the whole dissolves in hot water with the same colour. If, instead of water, hydrochloric acid is employed, the liquid is coloured at first a dirty yellow, then a red, with the formation of black resinous flocks, which dissolve in bisulphide of carbon with a splendid magenta colour. This colour cannot be withdrawn from the sulphide of carbon either by pure or by acidulated water.

Binitro-anthraquinon reacts energetically upon cyanide of potassium, forming, according to circumstances, violet-brown or orange-red compounds. If, according to Boettger and Petersen, binitro-anthraquinon is dissolved in 16 or 18 parts of concentrated sulphuric acid, and if heat is applied, at about the temperature of 200° C., there is an abundant disengagement of sulphurous acid, and the colour of the liquid changes from a yellowish-brown to a deep red-brown. The reaction becomes more and more brisk, so that it is necessary to withdraw the heat for some time. When the violence of the action has ceased heat is again cautiously applied, until the escape of sulphurous acid has discontinued.

The mass is allowed to cool, and is thrown into cold water, when it deposits deep reddish-brown flocks, which, after being filtered and washed, dissolve in dilute alkaline solutions with a deep violet-blue colour, and are re-precipitated on the addition of an acid. This substance may be purified by re-crystallisation from alcohol, when it is obtained in small agglomerated granules of a deep violet, or in brilliant incrustations of a brownish-violet with metallic reflections. This colour is sparingly soluble in water, to which it imparts the colour of peach-blossom. It dissolves freely in alcohol, ether, and glycerin, forming solutions of a splendid violet-red. It dissolves in acetic acid with a magenta-red, in sulphuric acid with a hyacinth-red, and in alkaline solutions with a violet-blue. It dyes cotton a violet, without mordants.

30. Artificial Isopurpurin.—This isomer of purpurin has been recently discovered by Auerbach in the product prepared by Gessert Bros., of Eberfeld, under the name of alizarin, with a yellow reflection, or purpurin, because it produces—both in dyeing with an aluminous mordant and as a steam-colour in printing—shades similar to those obtained with the natural purpurin from madder (see p. 247).

This so-called yellow alizarin or artificial purpurin appears in form of a slightly liquid homogeneous paste, containing 15 per cent of dry matter, and soluble in dilute caustic alkaline lyes, yielding a solution of a splendid reddish-violet colour.

To extract isopurpurin from this substance it is dissolved in ammonia, the solution is mixed with hydrate of baryta, and the precipitate formed is boiled with water as long as the filtered liquid has a red colour. From this aqueous solution the isopurpurin is precipitated with an acid, filtered, washed, and the same treatment is repeated. If the isopurpurin is precipitated with sulphuric acid, it may be isolated by treatment with alcohol, the precipitate composed of sulphate of baryta and of isopurpurin. The latter dissolves very readily.

Isopurpurin prepared in this manner, repeatedly purified with hydrate of baryta and crystallised from alcohol, has the same composition as the purpurin from madder.

Isopurpurin is of an orange-red, and presents all the properties of alizarin, but it dissolves in the hydrate of soda with a more violet-red colour. It is

readily soluble in alcohol, and moderately soluble in boiling water, from which it separates on cooling. It does not melt at 360°, but it begins to sublime at that temperature. In caustic alkalies it dissolves with a violet-red colour. In ammonia it dissolves with a reddish-brown. The solution in alkaline carbonates is likewise red, but with a decided brown shade. It is but very sparingly soluble in a saturated and boiling solution of alum. The liquid takes a yellowish-red tint, but without presenting in a high degree that beautiful red fluorescence which characterises similar solutions of purpurin. On cooling, the dissolved colouring matter is almost entirely separated out again. The barytic lake, of a violet red, is easily soluble in boiling water. The lime lake, which is of the same colour, is very sparingly soluble.

An alcoholic solution of isopurpurin, if examined in the spectroscope, shows bands of absorption in the orange and the green, and a faint one in the yellow. If the liquid is too concentrated all the spectrum disappears except the red.

On mordanted cotton isopurpurin gives shades similar to those produced by purpurin; the reds and roses border upon a scarlet; the violet is brownish; the browns and blacks are full; and all these colours resist boiling soap-lyes.

31. Anthrapurpurin.—We have already given (p. 327) a brief notice of the anthrapurpurin discovered by Mr. W. H. Perkin. We add the following particulars:—Crude artificial alizarin is dissolved in a dilute solution of carbonate of soda, and the liquid is agitated with alumina recently precipitated. The alizarin combines with the alumina to form a lake, whilst the anthrapurpurin remains in solution. The precipitate is filtered off, the filtrate heated to ebullition, and mixed with hydrochloric acid. The colouring matter thus thrown down is filtered, washed, and dried.

The anthrapurpurin obtained by this process is still very impure, containing anthraflavic acid and a substance which gives an orange colour with mordants of alumina. These impurities are in great part removed by repeated boiling in alcohol, in which anthrapurpurin is but slightly soluble. To obtain an absolutely pure product, the best method is to digest the substance with a boiling alcoholic solution of soda. The sparingly soluble soda-compound formed is collected upon a filter, and repeatedly washed with a dilute alcoholic solution of soda. The residue is then dissolved in water, boiled, and the colouring matter is precipitated by chloride of barium. The purple compound thus obtained is collected upon a filter, washed several times with hot water, and finally decomposed by boiling with carbonate of soda. The purple solution is filtered, and from the filtrate the anthrapurpurin is precipitated with hydrochloric acid. It is collected upon a filter, well washed, dried, and finally crystallised twice from glacial acetic acid, when it separates in orange needles. If boiled with alum it yields no special reaction, whilst its isomer, purpurin, yields a violet, fluorescent solution. From isopurpurin, with which it presents certain analogies, it is distinguished by its sparing solubility in alcohol, in which isopurpurin dissolves freely.

32. Aurin (Yellow Corallin, Rosolic Acid) is pronounced by Dale and Schorlemmer to be a mixture of different bodies. To prepare this substance in a state of purity the commercial product is dissolved in boiling alcohol, and alcohol saturated with ammoniacal gas is added. A crystalline compound of aurin and ammonia, almost insoluble in alcohol, separates out, whilst the impurities remain in solution. The precipitate is washed in alcohol and

exposed to the air, when the ammonia evaporates and pure aurin remains. Aurin, heated to 180° C. with alcoholic ammonia, yields red corallin.

According to H. Fresenius, the rosolic acid obtained by Caro and Wanklyn, on treating an acid solution of a salt of rosaniline with nitrous acid and boiling the residue, is not identical with the phenol-rosolic acid. He proposes for it the name of pseudo-corallin.

33. Derivatives of Resorcin.—If resorcin is heated to 195° C. with anhydrous phthalic acid, we obtain fluoresceine. It crystallises from alcohol in small deep brown crystals. If thrown down by acids from its potassic solution it takes the form of a brick-red powder. With ammonia it yields a red solution, which even when very dilute displays a magnificent green fluorescence. Fluoresceine dyes wool and silk a fine yellow without mordant.

In alkaline solution it is converted by zinc powder into colourless fluoresceine, which recovers its colouration under the influence of oxidising agents. If heated strongly with sulphuric acid and poured into water, it gives rise to a red deposit, which dissolves in alkalies with a blue colour, and is rendered blue by zinc-powder. The red liquid may be used for dyeing blue on the principle of the indigo-vat, but the colour is neither beautiful nor fast. Fluoresceine is in many respects analogous with litmus.

34. Derivatives of Hydroquinon.—If hydroquinon is heated to 130° to 140° C. with concentrated phthalic acid two products are formed: the phthalein of hydroquinon, which is colourless, and an isomer of alizarin, of a red colour, to which Grimm has given the name quinizarin.

To obtain the latter body the product of the reaction of phthalic acid and sulphuric acid is dissolved in alcohol, and water is added, when quinizarin is deposited in orange flocks, which when dried at 100° to 110° C. become red and crystalline. The ethereal and sulphuric solutions present a yellowish green fluorescence, similar to that of the munjistin of Stenhouse.

Grimm suggests that munjistin and quinizarin bear the same relation to each other as do purpurin and alizarin. Quinizarin melts at 192° to 193° C., and sublimes in feathery crystals. Its solution in the alkalies is blue; its ammoniacal solution and that formed with alkaline carbonates is more violet. It gives a blue-violet compound with magnesia, and a red-lake with alumina.

Quinizarin may be easily confounded with alizarin, and dyes mordanted cotton in the same manner.

- 35. Derivatives of Pyrocatechin.—If pyrocatechin is heated with anhydrous phthalic acid and with sulphuric acid, on adding water a greenish liquid is produced, which with potash gives a blue colouration that soon disappears. Baeyer thinks that this substance may be analogous to the colouring matter of logwood.
- 36. Gallein.—This colouring matter has been noticed on p. 508. The following additional particulars may be useful. Gallein dyes tissues mordanted with alumina and oxide of iron in the same manner as the red woods, but the shade is rather more blue. The colours are intermediate between those of peachwood and logwood. It is extremely probable that gallein belongs to the family of the tinctorial wood pigments, and that it is the first member of the series which has been artificially prepared.

Gallin produces the same shades as gallein, and shows a marked analogy with hæmatoxylin.

37. Nitrous Derivatives of Resorcin.—By the action of nitrous acid upon resorcin Weselsky has obtained colouring matters which in their brilliance and beauty rival the finest of the aniline colours, and which display phenomena of fluorescence in a splendour far surpassing all bodies previously observed. One of these compounds is formed by passing a current of nitrous acid into an ethereal solution of resorcin. It forms brown crystalline grains with a green metallic lustre, sparingly soluble in water, and rather more soluble in alcohol and acetic acid. Its solutions are of a deep cherry-red colour. In alkaline liquids it dissolves with a rich violet-blue. If the above substance is treated with concentrated nitric acid, with the aid of heat we obtain nitrate of tetrazoresorcin in fine garnet-red crystalline needles of great brilliance. They dissolve in water, ether, and alcohol with a pure indigo-blue colour. The discovery of a cheap source of resorcin is needed to render these colours practically available.

38. Cyanin.—I part of cinchonine or quinoidine is mixed with 3 parts of hydrates of potash or soda, and as much water as would be needed to dissolve the alkali with the aid of heat, and the mixture is distilled in an iron retort. Along with the watery vapours an oily liquid passes over and settles to the bottom of the water. This is crude chinoline, and amounts in quantity to 65 per cent of the cinchonin used. After removal of the water the chinoline is reclified. The portion passing over between 216° to 360° C. is suitable for the preparation of cyanin.

For a purple shade of cyanin I part of chinoline is mixed with I½ parts iodide of amyl. The mixture is brought to a boil, when it gradually takes a deep brown colour, and on cooling becomes a crystalline brown mass of hydriodate of amyl-chinoline. The product of the reaction is boiled for ten minutes with six times its weight of water, and when dissolved the liquor is filtered while still boiling.

The filtrate is placed in a boiler of enamelled iron, brought gradually to a boil, and mixed by degrees with an excess of ammonia. The boiling may be kept up for some hours with advantage, but the evaporated liquid must be replaced with a mixture of equal parts of common ammonia and distilled water. After boiling the mixture is allowed to cool, when the colouring matter is almost entirely precipitated, the supernatant liquor retaining scarcely a trace of colour. The whole is then filtered to separate the colouring matter, which dissolves in alcohol with a fine blue purple colour.

To prepare cyanin the following process may be employed. The brownish black crystalline mass above mentioned is moistened with five or six times its weight of boiling water, boiled for some time, and filtered. Upon the filter there remains a tarry mass, which dissolves in alcohol with a bright red colour, and may be employed as magenta. The filtrate is of a yellowish green colour and milky appearance. It is heated to boiling and mixed with a lye of caustic soda or potash containing one-fifth of its weight of the solid alkaline hydrate. The lye is added by degrees to the liquid, which is kept at a gentle boil until a quantity of alkali has been introduced equivalent to three-quarters of the iodine contained in the iodide of amyl employed. After boiling fifteen to thirty minutes, during which the liquid takes first a brick colour and then a green, leaflets of a deep blue colour begin to fall, and unite to a black resinous mass, which is cyanin. The colouring matter is filtered and washed with water, in which it is almost insoluble. If the filtrate is

brought again to a boil, and if the remaining fourth part of the caustic-lye is added, a black mass is thrown down, which is also cyanin, but which contains all the red colouring matter. This red would have been mixed with the whole of the cyanin if the total caustic-lye equivalent to the iodine of the iodide of amyl had been added at once. The last black precipitate dissolves readily in alcohol, forming a splendid purple-red solution. If this purple alcoholic liquid is filtered, there often remains on the filter a deep coloured mass, which dissolves in benzol with a fine emerald-green colour. The crude precipitate of cyanin dissolves in alcohol with a splendid blue colour, and can be crystallised from the solution.

According to the researches of Hofmann, Madler, and Merz, cyanin is not a simple substance, but a mixture of at least two homologous bodies, the one derived from chinoline, and the other from lepidine.

These two cyanins are very similar in their properties, and the colours which they produce upon textile fibres may be considered identical. The cyanin manufactured and sold by Mueller, of Basle, is chinolin-cyanin, whilst that of Menier, of Paris, is lepidin-cyanin, containing mere traces of chinoline.

In purity and beauty the blue shades produced by cyanin, especially upon silk, are unsurpassed. By artificial light they appear of a splendid violet. Unfortunately the colour is exceedingly fugitive, being destroyed in a few hours by exposure to the direct rays of the sun. No method of overcoming this drawback has yet been discovered, and in consequence cyanin has gradually disappeared from the market.

39. Dalleiochin (Quinine Green).—This colour has never become an article of commerce. It is prepared as follows:—

 Sulphate of quinine
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...
 ...<

These substances are allowed to react upon each other, and 125 parts of liquid ammonia are added. A greenish resinous matter is thus precipitated and is collected upon a filter. Quinine green is insoluble in water, benzol, and ether, but it dissolves in alcohol, wood-spirit, and glycerin. Acetic acid turns it to a blue shade: the mineral acids dissolve it with a brown colour, but on neutralisation the original colour is restored. Salt of tin decolourises the solutions. The alcoholic solution diluted with water dyes silk a green, which retains its tone by artificial light. Wool is dyed like silk. Cotton requires to be animalised with albumen. For printing, quinine green is mixed with albumen and the colour fixed by steaming. The shades produced are far inferior to those obtained with the aldehyd and iodine greens.

40. Aloes.—The following particulars may be superadded to the information found on p. 417:—

Pure aloetic and chrysammic acids are not commonly employed in dyeing and printing, but mixtures of these acids. In preparing the colour by Sacc's process, the solution of aloes in nitric acid is poured in a very slender-stream into cold water. Lindner heats in the water-bath r part of aloes with 60 parts of nitric acid until red vapours come off, and introduces then by degrees 9 parts more of aloes into the solution, evaporating to dryness when the reaction is over. The resulting mass, which is of a gold-yellow, is washed

on a filter and dried. The yield is 66 per per cent of the weight of the crude aloes employed. The aqueous solution is used directly for dyeing. Löwe digests without heat I part of aloes in 8 parts of nitric acid, and after having filtered the solution pours it into a large quantity of water. He also prepares chrysammic acid by evaporating a solution like the above down to one-half. He then adds \(\frac{1}{2}\) part of nitric acid, and concentrates afresh till crystals of oxalic acid appear, when he pours the whole into a large amount of water.

If instead of proceeding as above the concentrated nitric solution is mixed with excess of ammonia and the whole evaporated to crystallisation, chrysammid is obtained in small brilliant crystals.

A cheaper preparation may be made by dissolving 132 parts of aloes in 100 parts of boiling water and adding 80 parts of nitric acid. There is a brisk effervescence and a plentiful disengagement of gas. The acid is then neutralised with about 10 parts of soda-lye, of sp. gr. 1'12. Before making use of this preparation the mixture is slightly acidulated with hydrochloric or tartaric acid. The action of any deoxidising agent, especially protochloride (muriate) of tin changes red chrysammic acid and violet chrysammid into blue hydro-chrysammid. All the shades produced upon silk, wool, or cotton, ranging from red to violet or to cinnamon-brown are, in contact with reducing agents, converted to grey, blue-grey, greyish blue, olive-green, or moss-green. If silk and wool are plunged into a weak aqueous solution of chrysammic acid, and the bath is raised to a boil, the silk takes shades varying from rose to corinthe (a colour somewhat approaching that of dried currants), whilst wool is dyed a chestnut-brown, varying in intensity. Cotton unmordanted is not dyed; if prepared with alumina it takes a violet. If mordanted with iron it remains undyed. Linder's aloetic acid produces upon wool, unmordanted, a deep brown, which may be carried to a velvety black. Löwe's imperfect chrysammic acid yields upon wool reddish-brown shades. Linder's aloetate of soda (aloetic acid neutralised with soda) imparts to wool, unmordanted, a fine bluish-grey colour.

Chrysammid dyes silk and wool a grey, light or dark; with the addition of pink-salt the tone becomes greenish.

Upon silk chrysammid dyes a nut-brown; upon wool a yellow before steaming, and an olive-green after this operation.

When perchloride of tin is added we obtain a rusty yellow upon cotton, and a cinnamon-brown upon silk and wool.

With alum chrysammid yields, before steaming, a rusty yellow or buff upon silk and cotton, and a yellow upon wool. After steaming the cotton becomes a pearl-grey, the silk a drab, and the wool a bright "wood" colour.

According to Lindner, aloetic acid (aloes purple) is useful for fixing colours which in themselves are deficient in solidity. If, for instance, to parts of orchil are mixed with ½ part of aloes purple, previously dissolved in soda-lye, the colour of the orchil is unaffected by air and light, without any injury to its brightness. If in dyeing cotton goods with madder or fleur de garance a little aloes be added to the bath, the garnet-brown shades acquire a peculiar lustre.

41. Rufigallic Acid.—Gallic acid can be transformed into tannin by boiling with a very small quantity of arsenic acid, which undergoes no

alteration. Both tannin and gallic acid, if heated to 70° or 80° C. with concentrated sulphuric acid, yield by degrees a deep purple solution. This, poured into excess of water, deposits a 'reddish-brown powder, which is thrown upon a filter and freed from sulphuric acid by washing; 5 parts of sulphuric acid are required to 1 part of gallic acid or 1 of tannin. The product, which amounts to 66 per cent of the original matter, is rufigallic acid. It dissolves in sulphuric acid; with strong alkaline lyes it takes an indigoblue, and it forms a blackish-blue potash salt. In dilute lyes it dissolves with a violet colour; but it gradually separates out from the solution. If moistened with ammonia it takes a red colour. It dyes cotton goods mordanted with alumina and salts of iron in the same manner as alizarin. The shades are perfectly proof against soaping, but they are dull and deficient in purity.

Adulteration of Albumen.

Albumen is often adulterated with gum, dextrin, and starch. To detect these impurities I oz. of the sample is dissolved in lukewarm water. After some time the mass is stirred. If the liquid contain many white clots the quality is inferior; that shows that a notable quantity of the albumen has been coagulated by the employment of too high a temperature during evaporation. The solution is mixed with acetic acid, and some alcohol is added to the decanted acid liquid. If gum is present a precipitate is formed. Starch may be detected by adding a solution of iodine in water, which gives a blue-black colour. If the albumen contains sugar it is easily recognised by means of Fehling's test.

Dyeing Aniline Blacks on Cotton Yarn.

This process requires great care to prevent the blacks from becoming uneven and clouded. The cotton yarn, previously well boiled out, receives seven turns in a bath composed of 200 grms. of sulphate of copper for every kilo. of material dissolved in water slightly acidulated with hydrochloric acid. It is then well wrung out. Next it receives five turns at 50° C. in a bath containing 50 grms. hydrosulphate of soda per litre of water, and is next rinsed. It then receives seven turns in a bath of 10 litres of water, 180 grms. chlorate of potash, and 170 grms. of sal-ammoniac dissolved with the aid of heat, and then mixed with 480 grms. chloride of aniline. It is then stretched out very regularly in a hot drying-room at 24° C. for forty-eight hours. It then receives four turns at 30° C. in a bath containing 1 grm. bichromate of potash per litre, and is well rinsed and dried. If the blacks have a reddish tone they may be passed through a bath containing 1 litre of bleaching-liquor at 6° B. to 100 litres of cold water.

Printing-Ink for Use in Calico-Printing.

The following mixture gives fine blacks in the pigment-style: -

Venice turpenti					
Soft potash soa	p	 	 	 	 IO ,,
Olein					
Lamp-black	* 1	 	 	 	 6 ,,
Bleu de Paris		 	 	 	 I part.
Oxalic acid		 	 	 	 0.5
Water		 	 	 	 I .,

The turpentine is first heated along with the olein; then the soap is placed on a levigating-slab, and the mixture of turpentine and olein is gradually incorporated with it. When this is complete the lamp-black, previously ground and sifted, is worked in. Lastly, the Paris blue is gradually ground in, and the oxalic acid and water, which are previously mixed and slightly warmed. The Paris blue and oxalic acid may be replaced with a neutral extract of indigo.

New Iron Mordant.

Dissolve-

Chromate of	potash	 	 	 	4.5	200 grms.
Oxalic acid		 	 	 		200 ,,
Green vitriol		 ÷ +	 	 		6 kilos.
Water		 	 	 		6 litres.

New Aniline Red.

Acetate of aniline is mixed with ammoniacal oxide of copper and saturated with sulphuric acid, when a fine purple-red colour is developed. After concentration the liquid, on standing, deposits crystals of sulphate of ammonia, which are filtered off. The new aniline red remains then transparent.

Printing Aniline Colours on Calico.

A solution of gelatin is prepared, containing 50 grms. to the litre of water. Solution of bichromate is then added, drop by drop, till a straw-colour is produced. The aniline colour is then added, and the mixture thickened with dextrin or torrefied starch. After printing, the pieces are exposed for some hours to light, which renders gelatin insoluble when in contact with chrome. The gelatin may be replaced by a solution of casein in a small quantity of ammonia.

Use of Epsom Salts in Dyeing.

In dyeing wool for goods which are required to be "milled" the addition of Epsoms gives greater permanence to the aniline colours, especially *Primula* and methyl violets. The addition of sulphurous acid is also advantageous.

Test for Saffranin.

If a few particles of the suspected colour are mixed with 2 drops of concentrated sulphuric acid in a porcelain capsule, and stirred, a splendid blue colour immediately appears. The addition of 2 drops of water converts the blue to an emerald-green.

Cochineal-Red on Cotton.

To 10 lbs. of the yarn, &c., take 10 ozs. of tannin, and dissolve it completely in boiling water. Steep the goods over-night in this liquid. Prepare some red liquor at 12° Baumé, and put into a small tub a sufficient quantity to work 2 lbs. of cotton yarn. Work the yarn for ten minutes. Fill up the red liquor to its original quantity, and work 2 lbs. more, and so on until the whole of the cotton has been mordanted. It is then allowed to dry, with frequent turning. Piece-goods are winced for an hour in red liquor of the same strength. When

dry, the goods are passed through a boiling bath containing I lb. prepared chalk to every Io lbs. of cotton, and washed twice: I to I½ lb. of cochineal is extracted in water, the bath is heated to I22° F. with the addition of a little flavin, and the goods are worked therein, the temperature being slowly raised to the boiling-point.

Method of Determining Anthracen.

Dissolve I grm. of the sample of commercial anthracen in question in 45 cubic centimetres of glacial acetic acid, at the boiling-point, in a small flask. The solution, if needful, is filtered while boiling, and a solution of 10 grms, of chromic acid in 5 cubic centimetres of water and 5 cubic centimetres of glacial acetic acid, the liquid being kept at a gentle boil. The addition of this mixture is continued till a distinct and permanent yellowish-green colour appears, or till, after prolonged boiling, a drop of the liquid placed upon a clean silver coin produces a reddish spot. The whole is then diluted with 150 cubic centimetres of water, filtered after standing some hours, and the precipitate (chinon) is washed upon the filter, first with water, then with hot and very dilute potash-lye, and then again with water. It is next dried at 212° F., and weighed. After weighing, the chinon is removed from the filter. and the latter is weighed again. Thus the nett weight of the anthrachinon is obtained, to which o'or grm. must be added, that quantity having been dissolved and removed by the above-directed quantity of acetic acid and water. Commercial chromic acid, it must be remembered, often contains lead.

New Class of Colouring Matters.

Croissant and Bretonnière have patented a process for converting certain organic bodies into colouring matters. The process is applicable not merely to tannin, aloes, starch, and horn, which have a certain value, but to waste worthless bodies, such as moss, cellulose, sawdust, humus from decayed wood, &c. The principle employed is the dehydrogenation of the bodies by the action of sulphur at an elevated temperature, which the authors believe replaces the hydrogen. If it is required to convert bran into colouring matter it is placed in a small iron vessel, covered with a lid. Caustic soda and flower of sulphur are added in certain proportions, and the whole is made up into an homogeneous paste. The vessel is then placed in a furnace where it can be heated to 250° to 300° C. Sulphuretted hydrogen is given off in abundance. When the mixture is dry we find in the vessel, after cooling, a black, friable matter, perfectly soluble in water, to which it imparts a fine sap-green. The solution has a strong affinity for fibres, which it dyes without a mordant. One and the same body gives various tones of colour, according to the proportions of the mixture and the temperature applied. Certain substances—such as extracts of dye-woods, aloes, &c .- are converted at boiling-point, whilst woody fibre, bran, &c., require a higher temperature.

The following examples may be useful:-

I.	Aloes	 	 	 	3 kilos.
	Soda-lye, at 40° Baumé				
	Water				
	Flower of sulphur	 	 	 	3 kilos.

The mixture is boiled, and yields a lilac-grey. At higher temperatures a deep brown is produced.

This "normal sulphide" contains 70 litres soda-lye at 40° B., 65 litres of water, and 30 kilos. of sulphur. To dye cotton, a sufficient quantity of the product is dissolved in water at 60° C., and the goods are worked in this in the usual manner. They are then passed through boiling bichromate of potash solution, which fixes the colour.

Vat-Blue Ground, with a Red, Brown, Black, and White Pattern.

The goods are bleached, freed from chlorine with "antichlor," stiffened, and calendered. They are then printed with the following colours:—

For white:—10 parts verdigris are stirred up in acetic acid, the mixture diluted with water, and 4 lbs. of pipe-clay are well beaten up in this liquid. As soon as the whole is thoroughly incorporated 1 lb. of powdered gum arabic is added, allowed to dissolve, well stirred up, and water added sufficient to bring it to the consistence required for printing: \(\frac{1}{4}\) lb. of blue vitriol and \(\frac{1}{2}\) ozs. tartaric acid are then stirred in.

For the red:—2 lbs. pipe-clay are beaten up in red liquor at 10° Baumé; 3 lb. of ground gum arabic is added, and the mixture is allowed to stand at a gentle heat till all is dissolved; 3 ozs. of powdered blue vitriol are then well stirred in, and, lastly, a solution of 2 ozs. of verdigris in the smallest possible quantity of strong acetic acid. The whole is well stirred up, and is ready for use.

For a chocolate-brown:—Add to the mass, as directed for red, \(\frac{1}{2}\) lb. of iron liquor at 10° B.

For the black:—Dissolve \(\frac{1}{4}\) lb. of solid logwood extract in 6 lbs. of boiling water; cool, strain, and dissolve in the clear liquid \(\frac{1}{4}\) lb. of blue vitriol; 10 ozs. of powdered gum arabic are added, and the mixture is allowed to stand, with frequent stirring, till the gum is completely dissolved; 2 ozs. of verdigris are then dissolved in the smallest possible quantity of boiling acetic acid; the solution is added to the mixture, and 6 ozs. of iron liquor at 12° B. are finally stirred in.

These four colours are blocked in or printed with the perrotine, and the pieces are hung up for four days. They are then vatted to the shade desired, care being taken not to remove the resists by friction. The pieces are then passed through a dung-bath at 167° F., 15 to 20 lbs. of dung being allowed to each piece. Finally, the goods are dyed either with madder or artificial alizarin, the latter requiring no clearing. If alizarin is preferred, 1½ lbs. of the paste are used along with 1 litre of bran. If madder is used, 6 lbs. are required along with 3 lbs. bran and 1½ lbs. sumac. After dyeing, the goods are passed through a boiling bran-bath, rinsed, passed through weak chloride of lime, rinsed again, and dried.

Black and White on a Madder-Red Ground.

The pieces, duly bleached, are padded with red liquor at 12° Baumé, and dried at 66° F. After hanging three days they are printed with the following mixtures:—

Black.—			
Gum tragacanth		 	I2 OZS.
Starch			
Glue		 	8 ozs.
Boil up to a paste in water, and add	d		
Iron liquor		 	3 litres.
Nitrate of iron		 	I litre.
Make up the whole with water to 6	litres.		
Discharge White.—			
Gum tragacanth		 	I2 OZS.
Starch		 	ı 1b.
Glue		 	8 ozs.
Boil up to a paste, and add—			
Citric acid		 	2 lbs.

The pieces are then aged, dunged, rinsed, and dyed up in madder, taking 10 lbs. madder and 2 lbs. chalk per 60 yards. After dyeing, the goods are passed through a chlorine bath, taking 1 lb. chloride of lime for the above quantity. The pieces are then rinsed, passed through muriatic sours at \(\frac{1}{2} \) Baumé, and rinsed again. If, after rinsing, the goods are still acid, they are passed through a chalk bath, and rinsed again.

Dark Spirit Violet on Cotton Warps.

First Method, with Logwood.—Soften & 1b. gum tragacanth in water, and let it swell up to a jelly. Meantime dissolve & 1b. logwood extract in boiling water. Mix both solutions, make them up to 10 litres, boil, and stir till cold. Into the mixture stir & 1b. of crystallised bichloride of tin (perchloride), and add finally 1 & 02s. bichromate of potash in powder. The mixture is ready for use after being well stirred. The printed yarns are exposed to the air for a day, and are then rinsed without steaming.

Second Method, with Aniline Colours.—Soften 2 lbs. casein in water at 167° F., adding ½ lb. liquid ammonia. Dissolve 1 oz. aniline violet and ½ oz. crude magenta in water; mix with the casein, make up to 10 litres, and add 4 ozs. powdered bichromate of potash. The mixture can be used immediately for printing. The printed yarns are dried in the sun, and rinsed. For a darker shade more bichromate is required.

Blackley Orange is the trade name of a coal-tar colour manufactured by the well-known firm Levinstein and Sons, of Manchester. It is easily soluble in hot water. For printing on woollens or silks a concentrated solution in water is employed, without the addition of acids or mordants. In dyeing it is applied at a boiling-heat, with a slight addition of tartaric or acetic acid, or of the chloride of zinc. Large additions of acid destroy the colour. Blackley orange resists the action of the atmosphere better than most coal-tar colours, and its brightness is not injured by soap-lyes, warm or cold.

Dale's Patent Process for Printing and Dyeing with Aniline Colours.

First Method, applicable to Goods which are Printed in all Mauve, or have only very little Black.—The goods are bleached as if for the best madderwork, and printed with the following mixture. In machine-printing particular attention must be paid to have the colour-boxes quite clear, and especially free

from iron. The contact of iron must be avoided all through the process, or the colour will become a drab.

	hade for two									
	Gum Senega	I wat	er (1	o lb	s. pe	r gal	llon)			 ½ gal.
	Water									 1 ,,
	Tannic acid	(pure)							 20 ozs.
Light	Shade for tw	o Ma	uves	, or	3 W	. Ma	uve.			
	Gum-water									 ½ gal.
	Water									 1/2 ,,
	Tannic acid									
Dark S	hade for thr	ee M	auve	s, or	24 V	V. M	auv	· . —		
1	Gum-water									 d gal.
	Water									 I ,,
	Tannic acid						+ 1			 24 ozs.
Mediun	n Shade for	three	Mai	ives,	or I	o W	. Ma	uve.	_	
	Gum-water									 ½ gal.
	Water									
	Tannic acid									
	2									5500

The colour for covers is 2, 2½, or 3 ozs. per gallon of gum-water.

Dissolve the tannin in the water, and add to the gum-water. Sighten the dark shades with a little ground indigo, and the light ones with a little mauve or magenta. After printing age one night, or run the goods through the ageing-machine and let lie one night. Steam forty-five minutes, at I lb. pressure to the square inch. The goods are then ready for fixing. For the fixing process a wooden beck is divided into two parts: the first part is lined with lead, and contains a closed leaden steam-coil to heat the fixing liquor; at the end of each division is a pair of weighted rollers, to squeeze back as much as possible of the liquid: the second part of the beck contains cold water for rinsing. The first part of the beck is made up as follows:—

Water	 	 	 	 	 ı gal.
Tartar emetic	 	 	 	 	 2 ozs.
Glue					

The beck is filled three-fourths with this liquor, and heated from 170° to 190° F. Lower temperatures must be carefully avoided. The pieces travel through this liquid in three-quarters of a minute. The goods are well washed, and are then ready for dyeing.

For dyeing twenty pieces, 9/8, 25 yards each, put sufficient water in the beck, enter the pieces, raise the temperature to 120° F., add one quart of acetic acid at 8° Tw., and 20 ozs. of mauve paste, previously dissolved in 1 quart methylated spirit. Raise the temperature to a boil in seventy-five minutes, and boil fifteen to twenty minutes. Without the final boiling the whites will be soiled and the colours flat. Wash well, and dry. To clean the whites pass open through chloride of lime,—1 quart at 10° Tw., mixed with 18 gals. of water. Put in a beck containing 5 lbs. soap to 500 to 600 gals. water, and boil for eight to ten minutes; wash well, and finish.

For magentas the mordant and subsequent treatment are the same, and the goods are dyed up as follows:—For twenty pieces, 9/8, 25 yards, enter the

by the former method.

pieces, and raise the heat to 120° F.; add 4 lbs. of soap, dissolved in a little water. Dye in the same time and at the same heat as for mauve, and wath well. No clearing is generally required, but if the whites are not satisfactory they must be winced in soap, and on no account passed through bleaching-liquor. A wooden dye-beck must be used.

Second Method, for Single Colour Black and Mauve, or Dark Work.

360	ona Methoa, for Single Cold	our L	ouce	ane	L IVI C	uve,	Or.	Dark WO
No. 1	. Standard for Pale Shade	s.—						
	Gum Senegal water							½ gal.
	Water				. ,			1/2 79
	Tannic acid							8 ozs.
	Mauve to shade up to							12 ,,
No. 2	. Standard Medium							
	Gum-water and water as a	bove						
	Tannic acid							16 ozs.
	Mauve to shade up to			٠.				20 ,,
No. 3	. Standard, Dark.							
	Gum tragacanth water (1 I	b. pe	r gal	1.)	٠.			½ gal.

Mauve to shade up to 30 or 35 ,,

A small quantity of glycerin added to the printing colours is an improvement.

Print on madder-bleached cloth, without any further preparation; age one night and steam forty-five minutes at 1 lb. pressure to the inch, run through the fixing-beck, wash, and finish. Magenta by this process is not so good as

Artificial Orchil.

Tannic acid 24 ozs.

The following process has been patented in France (No. 97,641, Dec., 1872) by Messrs. Vogt and Henninger:-Toluene, or its monochloride or monobromide, is treated with concentrated sulphuric acid. To the acid mixture are added lime and carbonate of lime, so as to separate the excess of sulphuric acid as insoluble sulphate of lime. Or, in order to economise sulphuric acid, the acid mixture above mentioned may be allowed to act upon common salt, when hydrochloric acid is given off, and the residue contains sulphate of soda and the compound disulpho- or chloro- or bromosulpho- conjugated acids of toluene. A certain quantity of water is added, and the liquid containing the compound acids is decanted, and neutralised with lime. The solution then contains the disulphotoluate or chloro- or bromo-cresylo-sulphite of lime. which are then transformed into soda-salts by adding sulphate or carbonate of soda. The compound salts, when dry, are melted with double their weight of soda and (or?) potash, either under pressure or in open vessels, and furnish orcin, and the salicylates and cresylates of soda and (or?) potash. The reaction is effected at the temperature of 280° or 300° C.

The melted mass is then dissolved in water, saturated with hydrochloric or sulphuric acid, concentrated, and the alkaline chlorides or sulphates are removed by crystallisation. The mother-liquor contains orcin, which is transformed into orcein by the joint action of ammonia, lime, and atmospheric oxygen. (See p. 375).

Chemical Removal of "Burls" from Wool and Woollen Goods.

It is well known that the more powerful mineral acids,—especially the sulphuric, when diluted with water and aided by the action of heat, attack vegetable matters much more readily than wool. As early as 1853 Fenton and Crom patented the application of this principle for the destruction of cotton contained in the rags of mixed goods. The following year Izart and Lecoup took out a French patent for the application of the same principle to the destruction of the "burls," i.e., fragments of cotton, straw, thistle-seeds, and other vegetable matters entangled in wool. These burls, as is well known to practical men, are a source of considerable trouble. As they do not take the same colours as the wool, they have either to be plucked out of the pieces by hand, with the aid of peculiarly-constructed tweezers, or colour-mixtures—known as "burling-inks"—are applied to the spots with a blunt quill, or—as especially the case with black broadcloths, doe-skins, &c.—the entire pieces have to be "burl-dyed," i.e., submitted to a cotton-dyeing process.

The procedure of Izart, as modified in accordance with the results of experience, consists in steeping the wool, woollen yarn, or pieces, in a bath of dilute sulphuric acid at 3° to 4° Baumé. It is then drained in a centrifugal machine, and finally heated to 100° C. in a drying-stove, for a suitable time. The burls are thus destroyed, and the wool, being freed from all residual acid by thorough washing, is submitted to the ordinary manufacturing routine.

An experimental investigation has recently been carried on by Messrs. Duclaux, Lechartier, and Raulin, as to the limits of time, temperature, and concentration, within which this procedure is at once safe and efficacious. It has been proposed to use baths of earthy and metallic salts, zinc, tin, alum, &c., prior to the acid bath, with the notion of protecting the wool against any corrosion or alteration of its properties. Carefully executed experiments proved—as any judicious tinctorial chemist would have anticipated—that these additions had not the slightest effect in protecting the wool, and exerted, further, a very detrimental action on the subsequent dyeing operations. A variety of acids and acid salts, both mineral and organic, also chlorine and its oxygen compounds, were tried in comparison with sulphuric acid. The lastmentioned body, however, was found incontestably preferable.

Drainage in the hydro-extractor (centrifugal machine, or "whizzer") was proved to be quite indispensable. The following table shows the limits of temperature, time, and concentration of acid, within which the operation can be successfully conducted.

Temperature of Stove.	Acid for an Expe	osure of Two	Hours	Ditto for Half an Hour in Stove.
80° C.	1 lit. to 4 lit. (per 100 lit	res water)	3 to 7 litres.
110° C.	I lit. to 3 lit.	5 2	9.1	1½ lit. to 4½ lit.
150° C.	lit. to I lit.	23	9.9	I lit. to 11 lit.

Below these limits the burls are not destroyed, whilst above them the wool is attacked, and its affinity for mordants and colours seriously modified. After the stoving, the wool is passed through a weak bath of carbonate of soda, and is then thoroughly rinsed in pure water.

Corallin.

According to the recent investigations of Commaille, corallin is produced between 115° and 150° C., but more rapidly and plentifully at the latter

temperature, at which 100 parts of phenol yield, in six hours, 26 parts of corallin. From the mother-liquor 72 per cent of the oxalic acid employed can be recovered, whilst the sulphuric acid is found to have totally disappeared. Commaille considers that yellow corallin is not, as commonly supposed, an acid, and that red corallin is not the amid of the yellow. The proportion of oxalic acid employed is far too large. Corallin does not form definite metallic compounds.

Hydrometer Tables.

Baumé's scale for líquids heavier than water is graduated from o° to 72°. Its relation to direct specific gravity is shown in the following table:—

			0	
o°	= 1.000		39° =	I°345
3	1.030		42	1.385
6	1.041		45	1.421
9	1.023	į	48	1.462
12	1.086		51	1.202
15	1.100		54	1.221
18	1.134	İ	57	1.600
21	1.190		60	1.652
24	1.188		63	1.708
27	1.319		66	1.767
30	1.246		69	1.831
33	1.277		72	1.000
36	1.310	1		

The scale for liquids lighter than water extends from 10° to 40°, the lowest number representing the specific gravity of water, and the higher ones those of lighter liquids.

IO°	-	1.000		26°	=	0.001
II		0.893		27		0.896
12		0.386		28		0.890
13		0.080		29		0.885
14		0.973		30		0.880
15		0.962		31		0.874
16		0.000		32		0.869
17		0.924		33		0.864
18		0'948		34		0.859
19		0.945	1	.35		0.854
20		0.936		36		0.849
21		0.030		37		0.844
22		0.034		38		0.839
23		0.018		39		0.834
24		0.013		40		0.830
25		0.002				

Beck's scale, for liquids heavier than water, runs from 1°, which is slightly above the specific gravity of water, to 70°. It is a most inconvenient scale.

I° =	1.0029	1	5° =	1.0303
2	1.0110		6	1.0366
3	1.0190	1	7	1.0429
4	1.0241	1	8	1.0494

9"	=	7:0550	1	40°	=	Tioons
10	_	1.0559				1.3077
		1.0622		41		1.3148
11		1,0203		42		1.3281
		1.0759	1	43		1.3386
13		1.0828		44.		1.3492
14		1.0897		45		1.3200
15		1.0968		46		1.3710
16		1.1030		47		1.3851
17		1.1111		48		1.3934
18		1.1184		49		1.4020
19		1.1528		50		1.4162
20		1.1333		5 I		1.4286
21		1.1400		52		1.4402
22		1.1486		53		1.4530
23		1.1262	1	54		1.4655
24		1.1644	1	55		1.4783
25		1.1724		56		1'4912
26		1,1800		57		1.5044
27		1.1888		58		1'5179
28		1.1973	1	59		1.2312
29		1.2057		бо		I.2424
30		1.2143		61		1.5596
31		1.2230		62		1.5741
32		1.5310		63		1.2888
33		I'2409	1	64		1.6038
34		1.2500	1	65		1.6190
35		1.2593		66		1.6346
36		1.2687		67		1.6505
37		1.2782		68		1.6667
38		1.2879		69		1.6832
39		1.2977		70		1'7000
-		2,1	1			,

Cartier's scale, for liquids lighter than water, runs from 10° = water to 44°. Its relation to direct specific gravity is shown in the following table:—

IO°	=	1,000	1	24°	==	0'903
II		0.993	1	25		0.897
12		0.985	1	26		0.891
13		0'977	1	27		0.885
14		0.970		28		0.879
15		0.963	1	29		0.872
16		0.956	1	30		0.867
17		0.040	1	31		0.862
18		0.942	1	32		0.856
19		0.932		33		0.821
20		0.030		34		0.845
21		0'922		35		0.840
22		0.019	1	36		0.832
23		0.000		37		0.830

38° =	0.825	42°	= 0.804
39	0.813	43	0.799
40	0.814	44	0.494
41	0.809		

The direct scale of specific gravity assumes water to be 1, or 1'000, all heavier liquids requiring larger numbers, and all lighter ones numbers smaller than unity. This scale shows at once the weight per gallon of any liquid, the two first figures to the left hand representing pounds avoirdupois, and the two or more following to the right being decimal fractions of a pound. Thus if a sample of double muriate marks 1'450, a gallon of it weighs 14½ lbs.

Twaddell's scale makes water = 0, and the strongest oil of vitriol = 170°. Unlike direct specific gravity, it extends only to liquids heavier than water. For greater accuracy the scale is arranged on a set of six instruments, numbered progressively upwards. Thus a No. I Twaddell ranges from 0 to 32°.

The relation between Twaddell's scale and direct specific gravity is very simple. To convert a degree of Twaddell into the corresponding degree of direct specific gravity, multiply by 5 and add 1:000 to the product. Thus if a bleaching-liquor marks 7° Tw., its specific gravity is 7

A sample of single aquafortis marks 33° Tw. Its specific gravity is then-

If the specific gravity has been taken the degree of Twaddell may be found by reversing this rule, subtracting 1.000, and dividing the remainder by 5. Thus a sample of double aquafortis marks specific gravity 1.350. Its degree on Twaddell's scale will be—

1'350 1'000 5) 350 70° Tw.

In some hydrometers, graduated for direct specific gravity, the first figure is omitted. On such water marks o°, and the above-mentioned sample of double aquafortis 350°. A peculiar hydrometer—called the ammonia-glass or ammonia-meter—is used in some districts for the sale of ammonia. It ranges from 10° (= water) to 45°, representing the lightest liquors. It very nearly agrees with Baumé's light glass. Hydrometers give inaccurate results if applied to—

- a. Hot liquids.
- b. Glutinous liquids, solutions of gum, starch, size, &c.
- c. Effervescing liquids.
- d. Liquids holding solid matters in suspension.

Hot liquids should be allowed to cool, or, if it be necessary to observe their specific gravity at elevated temperatures, a comparative trial should be made on the liquid while hot, and on a portion when cold, so that the indication may be corrected. If it be needful to take the specific gravity of any liquid coming under the heads b, c, and d, a gallon should be accurately weighed.

In chemical, dye, and print works, where hydrometers are placed in the hands of foremen for frequent use, they should be regularly brought at some stated time to the laboratory for verification.

Thermometer Scales.

To convert Centigrade (Celsius) into Fahrenheit.—If the temperature be above the freezing-point of water (32° F. = 0° C.), multiply by 9, divide by 5, and add 32 to the quotient. If it be below freezing-point (32° F. = 0° C.), but above 0° F. (= -18° C.), multiply by 9, divide by 5, and subtract the result from 32° . If below -18° C. (= 0° F.), multiply by 9, divide by 5, and subtract 32° from the result.

Reaumur's scale, in which the boiling-point of water is made 80°, and the freezing-point, as in the Centigrade, o°, is still used in many German dye and print works.

To convert Reaumur into Centigrade, whether above or below freezing-point. multiply by 5 and divide by 4.

To convert Centigrade into Reaumur, multiply by 4 and divide by 5.

To convert Reaumur into Fahrenheit, or vice versa, the rules above given for the conversion of Centigrade into Fahrenheit, &c., will apply, 4 being used respectively as multiplier or divisor instead of 5.

Decimal or "Metric" Weights and Measures.

Measures of Length.

Millimetre = 0.03937 inch.

Centimetre = 0.393708 ,,

Decimetre = 3.937079 inches.

Metre = 39.370790 inches.

 $_{11} = 3.2808992$ feet.

" = 1.093633 yards.

Decametre = 32.808992 feet.

Hectometre = 328.08992 ,,

Kilometre = 3280.8992 ,,

,, = 1093.633 yards.

Myriametre = 10936.33 ,,

= 6.2138 miles.

English inch = 2.539954 centimetres.

,, foot = 3.0479449 decimetres.

,, yard = 0.91438348 metre.

, fathom = 1.82876696 metres.

" furlong = 201°16437 . ",

,, mile = 1609.3149

Superficial Measures.

Square millimetre = $\frac{1}{648}$ of a square inch.

,, ,, = 0.00155 ,, ,,

```
Square centimetre = 0.155086 ,,
        " decimetre = 15.5086 square inches.
        ,, = 0'10769 square foot.
        ,, metre or centiare = 1550.86 square inches.
            ,, ,, = 10.7698 ,, feet.
       12 39
                     " = 1·196033 " yards.
     Are = 1076.98 square feet.
     ,, = 119.6033 ,, yards.
      ,, = 0.098845 \text{ rood}.
     Hectare = 11960'33 square yards.
       = 2.471143 acres.
     Square inch = 645'109201 square millimetres.
      ", ,, = 6.45109 ,, centimetres.
       ,, foot = 9.2903 square decimetres.
        " yard = 0.836097 metre.
     Acre = 0.404671 hectare.
               Measures of Capacity.
Cubic millimetre = 0.000061029 cubic inch.
 ,, centimetre = 0.061029 ,, ,,
 ,, (millilitre) = 15.438395 grain measures.
ro cubic centimetres = 0.61029 cubic inch.
  ,, (centilitre) = 154.38395 grain measures.
100 cubic centimetres = 6'1029 cubic inches.
  ", (decilitre) = 1543.8395 grain measures.
1000 cubic centimetres = 61.0295688 cubic inches.
   " (litre) = 15438·395 grain measures.
       ,, ,, = 1.760773 imperial pints.
,, = 0.2200967 ,, gallon.
Decalitre = 610.295688 cubic inches.
   ,, = 2.2000668 gallons.
Hectolitre = 3.5317 cubic feet.
   ,, = 22.009688 gallons.
Cubic metre, stere, or kilolitre = 1.308 cubic yards.
   " = 35'3171 cubic feet.
" = 220'09688 gallons.
```

Myrialitre = 353'171 cubic feet.

Fluid ounce = 283.384 cubic centimetres.

Pint = 0.567932 litre.

Quart = 1.135864 litres.

Gallon = 4.54345797 litres.

Cubic inch = 16.3855 cubic centimetres.

" foot = 28.3159 " decimetres.

", yard = 0.764520695 cubic metre.

Weights.

Milligramme = 0.015438395 grain. Centigramme = 0.15438395 ,, Decigramme = 1.5438395 grains. Gramme = 15.438395 grains.

,, = 0.643 pennyweight.

" = 0.03216 oz. troy.

,, = 0.03527 oz. avoirdupois.

Decagramme = 154'38395 grains.

,, = 5.64 drams avoirdupois.

Hectogramme = 3.2154 ozs. troy.

,, = 3.527 ozs. avoirdupois.

Kilogramme = 2.6803 lbs. troy.

,, = 2.2054 lbs. avoirdupois.

Myriagramme = 26.803 lbs. troy.

,, = 22.05486 lbs. avoirdupois.

Quintal metric (100 kilos.) = 220.5486 lbs. avoirdupois.

Tonne metric (1000 kilos.) = 2205'486 lbs. avoirdupois.

Ton = 1015.649 kilos.

Hundredweight = 50.78245 kilos.

Quarter = 12.6956144 kilos.

Pound = 453.4148 grammes.

Ounce = 28.3375

Dram = 1.77108 " Pound troy = 373'096 grammes.

Ounce ,, = 31.0913 ,,

Pennyweight = 1.55457 ,,

Grain = 0.054773 ,,

Apothecaries' dram = 3.8869 grammes.

Scruple = 1.29546 grammes.

BIBLIOGRAPHY.

Coal-Tar.

- I. Examen des Matières Colorantes Artificielles dérivées du Goudron de Houille, par E. Kopp, première partie (Extrait du Moniteur Scientifique du Docteur Quesneville).
- 2. Ib., seconde partie.
- International Exhibition, 1862. Reports by the Juries. Class II., Section A., Chemical Products and Processes; Reporter, A. W. HOFMANN.
- 4. GAULTIER DE CLAUBRY. Rapport sur les Etablissements de la Société de Carbonisation de la Loire. Bulletin de la Société d'Encouragement. Octobre, 1862.
- F. ZIMMERMANN. Die Mineralöl-und Paraffin Fabrikation in der Provinz Sachsen, Zeitschrift für das Berg-Hütten-und Salinenwesen in dem Preussischen Staate, t. xiii., p. 62 (1865).
- 6. G. LUNGE. Die Destillation der Steinkohlentheers und die Verarbeitung der damit Zusammenhängenden Nebenproducte. Brunswick, 1867.
- 7. DEPOUILLY FRERES. Bulletin de la Société Industrielle de Mulhouse, 1865, pp. 217, 299.
- 8. W. H. PERKIN. Chemical News and Journal of Physical Science,
- 9. Th. Chateau. Couleurs d'Aniline, d'Acide Phénique et de Naphtaline.
 Paris, 1868.
- ro. A. Kekule. Chemie der Benzolderivate oder der Aromatischen Substanzen. Erlangen, 1867.
- II. Exposition Universelle de 1867. Rapports de Jury International, &c., t. vii., p. 223.
- Dr. Max Vogel. Die Entwicklung der Anilin-Industrie. Die Anilinfarben, ihre Entstehung, Herstellung und Technische Verwendung. Leipzig, 1866.
- 13. REIMANN. Aniline and its Derivatives. English Edition. By WILLIAM CROOKES, F.R.S., &c. London, 1868.
- A. JORDAN. Das Anilin und die Anilinfarben. Weimar, 1866. Appendice, 1870.
- T. H. Oppler. Theorie und Praktische Anwendung von Anilin. Berlin, 1866.
- 16. GIRARD et DE LAIRE. Traité des dérivés de la Houille, &c. Paris, 1872.
- 17. R. Wagner. Handbook of Chemical Technology. English Edition. By William Crookes, F.R.S., &c. Pp. 568 to 616. London, 1872.

Phenic Acid, its Homologues and Derivatives.

- 1. Runge. Poggendorff's Annalen, t. xxxi., p. 69; t. xxxii., p. 308.
- 2. LAURENT. Annales de Chimie et de Physique, troisième série, t. iii., p. 195.
- 3. GERHARDT. Revue Scientifique, t. x., p. 210.
- 4. Bobœuf. De l'Acide Phénique, de ses Solutions Aqueuses et du Phénol Solide. Deuxième Edition. Paris.
- 5. E. Kopp. Moniteur Scientifique, t. ii., p. 823.
- 6. CALVERT. Zeitschrift für Chemie, 1865, p. 530.
- 7. KEKULE. Zeitschrift für Chemie, 1867, p. 197.
- 8. ,, Chemie der Benzolderivate, p. 479.
- 9. BERTHELOT. Comptes Rendus, t. Ixviii., p. 539.
- 10. Church. Chemical News, 1871, p. 173.

Picric Acid and its Nitro-Products.

- BALARD. Rapport sur la Fabrication de l'Acide Picrique. Bulletin de la Société d'Encouragement. Mai, 1862.
- 2. Welter. Annales de Chimie, t. xxix., p. 301.
- 3. CHEVREUL. Annales de Chin ie, t. lxxii., p. 113.
- 4. Dumas. Annales de Chimie et de Physique, t. liii., p. 178.
- 5. , Annales de Chimie et de Physique, troisième série, t. ii., p. 228.
- 6. LAURENT. Annales de Chimie et de Physique, troisième série, t. iii., p. 221.
- 7. HOFMANN. Annal. der Chemie und Pharm., t. xlvii., p. 72.
- 8. STENHOUSE. Annal. der Chemie und Pharm., t. lvii., p. 87.
- 9. Hofmann. Report on Chemical Products and Processes, p. 135.
- 10. GUINON. Dictionnaire des Arts et Manufactures. Supplément, p. 608.
- II. CAREY LEA. Silliman's American Journal, second series, vol. xxvi., p. 279; vol. xxvi., p. 180. Répertoire de Chimie, Pure, t. i., p. 227.
- 12. MÜLLER. Zeitschrift für Chemie, 1865, p. 189.
- 13. HLASIWETZ. Annal. der Chemie und Pharm., t. cx., p. 289.
- 14. BAYER. Jahresbericht d. Chem. von Will, &c., 1859, p. 458.
- 15. FRITZSCHE. Annal. der Chemie und Pharm., t. cix., p. 247.
- 16. ZULKOWSKY. Isopurpurates. Dingler's Polytechn. Journal, t. cxc., p. 49.
- 17. H. GRUNER. Erdmann's Journ. f. Pract. Chem., t. cii., p. 222.
- 18. F. Springmuhl. Grothe's Musterzeit, 1871, No. 23.

Rosolic Acid, Corallin, &c.

- RUNGE. Annalen der Physik von Poggendorff, t. xxxi., pp. 65, 512;
 t. xxxii., pp. 308, 323.
- 2. TSCHELNITZ. Dingler's Polytechn. Journal, t. cl., p. 467.
- 3. A. SMITH. Chemical Gazette, 1858, p. 20. Répertoire de Chimie Appliquée, 1859, t. i., p. 163.
- 4. Hugo Müller. Quarterly Journal of the Chemical Society, vol. ii., p. 1.
 Répertoire de Chimie Appliquée, t. ii., p. 96.
- 5. Dusart. Répertoire de Chimie Appliquée, t. ii., p. 207.
- 6. JOURDIN. Répertoire de Chimie Appliquée, t. ii. (Juin, 1861), p. 216.
- 7. Kolbe et Schmidt. Annalen der Chemie und Pharm., t. cxix., p. 169.
- 8. Guinon, Marnas, et Bonnet. Répertoire de Chimie Appliquée, 1862, p. 450.

- SCHÜTZENBERGER et SENGENWALD. Jahresbericht der Chemie von Will, 1862, p. 412.
- IO. SCHÜTZENBERGER et PARAF. Comptes Rendus de l'Académie, 1862, t. liv., p. 197.
- II. KORNER. Annal. der Chemie und Pharm., t. cxxxvii., p. 203.
- 12. WANKLYN and CARO. Zeitschrift für Chemie, 1866, p. 511.
- 13. CARO. Zeitschrift für Chemie, 1866, p. 563.
- 14. BINDER. Répertoire de Chimie Appliquée, 1863, p. 54.
- 15. Perkin and Duppa. Chemical News, June, 1861, p. 351.
- 16. Pelouse et Fremy. Traité de Chimie, troisième édition, t. vi., p. 295.
- 17. Dale et Schorlemmer. Berl., 1871, pp. 574, 971.
- 18. H. FRESENIUS. Journ. für Prakt. Chemie, t. iii., p. 477.
- 19. KIELMEYER. Moniteur Scientifique, Septembre, 1872, p. 740.
- 20. F. Fol. Répertoire de Chimie Appliquée, t. iv., p. 179.
- 21. REIMANN'S Färber. Zeit., 1871, pp. 18, 50 (Jaune Campo-Bello).

Phenicienne and other Phenyl Browns.

- I. Roth. Bulletin de la Société Industrielle de Mulhouse, 1864, t. xxxiv..
- 2. E. Dolfuss. Rapport sur, &c., id., t. xxxiv., p. 500.
- 3. ALFRAISE. Brevet No. 60,358, du 8 Octobre, 1863.
- 4. Monnet. Bulletin de la Société Industrielle de Mulhouse, Octobre, 1861.
- 5. Dullo. Deutsche Industriezeitung, 1865, p. 193.
- 6. Bolley. Schweiz. Polytechn. Zeitschrift, 1869, p. 140.

Cresylol.

- I. WILLIAMSON and FAIRLIE. Annal. der Chemie und Pharm., t. xcii., p. 319.
- 2. Duclos. Annal. der Chemie und Pharm., t. cix., p. 135.
- 3. AD. WURTZ. Moniteur Scientifique, 1870, p. 547.

Binitrocresylol.

I. MARTIUS et GRIESS. Zeitschrift der Deutsch. Chemisch. Gesellschaft, 1869, p. 206.

Trinitrocresylol.

 KELLNER et BEILSTEIN. Annal. der Chemie und Pharm., t. cxxviii., p. 164.

Benzol, its Homologues and Derivatives.

- I. FARADAY. Phil. Transactions, 1825, p. 440. Poggend. Annal., t. v., p. 306.
- 2. MITSCHERLICH. Poggend. Annal., t. xxi., p. 231. Annal. der Chemie und Pharm., t. ix., p. 39; t. xxxi., p. 625; t. xxxiii. p. 224; t. xxxv., p. 370.
- 3. HOFMANN. Annal. der Chemie und Pharm., t. lv., p. 200.
- 4. Warren de la Rue and Müller. Journal für Prakt. Chem., t. xxii., p. 300. Jahresbericht der Chemie, 1856, p. 606.
- 5. FREUND. Annal. der Chemie und Pharm., t. cxv., p. 19.
- 6. Wohler. Annal. der Chemie und Pharm. t. cii., p. 125.
- MANSFIELD. Chem. Soc. Journ., vol. i., 1849, pp. 244 to 268. Chem. Coll. Reports, 1849, pp. 227 to 251.

- 8. Church. Annal. der Chemie und Pharm., t. civ., p. 111.
- 9. H. KOPP. Annal. der Chemie und Pharm., t. xcviii., p. 369.
- 10. Church and Perkin. Journal für Prakt. Chimie, t. xxxvi., p. 93; t. lvii., p. 177.
- II. Coupier. Bulletin de la Société Industrielle de Mulhouse, 1869, p. 259.

Toluol.

- PELLETIER and WELTER. Annal. der Chemie und Pharm., t. xxii., p. 150;
 t. xxviii., p. 297.
- CAHOURS. Pharm. Centralblatt, 1850, p. 344. Annal. der Chemie und Pharm., t. lxxvi., p. 286.
- 3. DEVILLE. Annal. der Chemie und Pharm., t. xliv., p. 305.
- 4. VÖLKEL. Annal. der Chemie und Pharm., t. Ixxxvi., p. 335.
- 5. E. Kopp. Comptes Rendus, 1849, p. 149. Gmelin, Handb., t. vi., p. 174.
- 6. Mansfield. Annal. der Chemie und Pharm., t. lxix., p. 176.
- 7. CANNIZARO. Annal. der Chemie und Pharm., t. xc., p. 252; t. xcvi., p. 246.
- 8. WARREN DE LA RUE and MÜLLER. Journ. für Prakt. Chemie, t. lxx., p. 300.
- 9. C. M. WARREN. Zeitschrift für Chemie, 1865, p. 666. Journal für Prakt. Chemie, t. xcvii., p. 50.
- 10. FITTIG and TOLLENS. Annal. der Chemie und Pharm., t. cxxxi., p. 304.
- II. COUPIER. Bulletin de la Société Industrielle de Mulhouse, 1864, p. 259.
- 12. ROSENSTIEHL. Bull. de la Sociéte Industrielle de Mulhouse, 1868, p. 194.
- 13. BERTHELOT. Bull. de la Société Industrielle de Mulhouse, 1869, p. 194.

Xylol.

- I. CAHOURS. See Toluol.
- 2. VÖLKEL. See Toluol.
- 3. WARREN DE LA RUE and H. MÜLLER. Journ. für Prakt. Chemie, t. lxx., p. 300. Annal. der Chemie und Pharm., t. cxx., p. 339.
- 4. H. MÜLLER. Zeitschrift für Chemie, 1864, p. 161.
- 5. Beilstein. Annal. der Chemie und Pharm., t. cxxxiii., p. 32.
- FITTIG. Annal. der Chemie und Pharm., t. cxxxiii., p. 47; t. cxxxvi., p. 303.
- 7. BECHAMP. Comptes Rendus, t. lix., p. 47.

Cumol.

- Gerhardt and Cahours. Annal. der Chemie und Pharm., t. xxxviii., p. 88.
- 2. ABEL. Annal. de Chemie und Pharm., t. lxiii., p. 308.
- 3. Mansfield. Annal. der Chemie und Pharm., t. lxix., p. 179.
- 4. MITTHAUSEN. Journ. für Prakt. Chemie, t. lxi., p. 79.
- 5. Church. Journ. für Prakt. Chemie, t. lxv., p. 383.
- 6. WARREN DE LA RUE and MÜLLER. See Xylen,

Nitrobenzol.

- 1. MITSCHERLICH. Annal. der Chemie und Pharm., t. xii., p. 305.
 - 2. MULDER. Journ. für Prakt. Chemie, t. xix., p. 375.

Binitrobenzol.

- I. DEVILLE. Journ. für Prakt. Chemie, t. xxv., p. 353.
- 2. Muspratt and Hofmann. Annal. der Chemie und Pharm., t. lvii., p. 214.

Nitrotoluol.

- 1. DEVILLE. Journ. für Prakt. Chemie, t. xxv., p. 353.
- 2. GLENARD and BOUDAULT. Journ. für Prakt. Chemic, t. xxxiii., p. 459.
- 3. JAWORSKY. Zeitschrift für Chemie, t. viii., p. 225.
- 4. KEKULE. Zeitschrift für Chemie, t. x., p. 225.
- 5. F. BEILSTEIN and A. KUHLBERG. Zeitschrift für Chemie, t. xii., p. 521

Binitrotoluol.

- I. H. DEVILLE. See Nitrotoluen.
- 2. CAHOURS. Comptes Rendus, t. xxiv., p. 555.

Trinitrotoluol.

I. WILBRAND. Annal. der Chem. und Pharm., t. cxxviii., p. 178.

Nitroxylol.

1. DEUMELANDT. Zeitschrift für Chem., 1866, p. 21.

Industrial Preparation of Nitrobenzol.

- I. MANSFIELD. Le Technologiste, t. x., 1848.
- 2. Collas. Secret des Arts par le Docteur Quesneville, 1851, Nos. 5 and 6.
- 3. DEPOUILLY FRERES. Bulletin de la Société Industrielle de Mulhouse, 1865, p. 217.
- 4. W. H. PERKIN. Moniteur Scientifique, 1869, pp. 145, 209, 257.

Aniline and its Derivatives.

- I. Unverdorben. Annal. der Physik, t. viii., p. 397.
- 2. FRITZSCHE. Annal. der Chem. und Pharm., t. xxxix., pp. 76, gr.
- 3. Runge. Annal. der Physik, t. xxvi., pp. 67, 513.
- 4. ZININ. Annal. der Chem. und Pharm., t. xliv., p. 283.
- HOFMANN. Annal. der Chem. und Pharm., t. xlvii., p. 37; t. lii., p. 56;
 t. liii., pp. 1, 57; t. lxvii., pp. 61, 129, 205; t. lxx., p. 129; t. lxxix., p. 11.
- Muspratt and Hofmann. Annal. der Chem. und Pharm., t. liii., p. 221;
 t. liv., p. 27;
 t. lxiì., p. 200.
- 7. BECHAMP. Ann. de Chimie et de Physique, troisième série, t. xlii., p. 186.
- 8. GOTTLIEB. Annal. der Chem. und Pharm., t. lxxxv., pp. 17, 265.
- 9. Wohler. Annal. der Chem. und Pharm., t. cii., p. 127.
- IO. H. SCHIFF. Annal. der Chem. und Pharm., 't. ci., 102; and Untersuchungen über Metallhaltige Anilinderivate. Berlin, 1864.
- 11. SCHEURER-KESTNER. Répert. de Chimie Appliquée, t. iv., p. 121.
- 12. BEILSTEIN. Annal. der Chem. und Pharm., t. ciii., p. 242.
- GREVILLE WILLIAMS. Repertory of Patent Inventions. January, 1860.
 Zeitschrift für Chem., 1864, p. 315.
- 14. RICHE and BERARD. Jahresbericht, 1863, p. 428.
- 15. GIRARD and DE LAIRE. Monit. Scientifique, t. ix., p. 245.

- 16. BERTHELOT. Annal. de Chim. et de Phys., troisième série, t. xxxviii., p. 63; t. lviii., p. 446.
- 17. JUNCADELLA. Annal. der Chem. und Pharm., t. cx., p. 254.
- 18. CH. BARDY. Monit. Scient., 1870, p. 553.

Toluidine and its Derivatives.

- 1. MUSPRATT and HOFMANN. Annal. der Chem. und Pharm., t. liv., p. 1.
- 2. A. W. HOFMANN. Annal. der Chem. und Pharm., t. lxvi., p. 144; t. lxxiv., p. 172.
- 3. WILSON. Annal. der Chem. und Pharm., t. lxxvii., p. 216.
- 4. H. MÜLLER. Jahresbericht, 1864, p. 423.
- 5. BRIMMEYR. Dingl. Polytech. Journ., t. clxxiv., p. 461. Zeitschrift für Chem., 1865, p. 513.
- 6. Grafinghoff. Journ. Prakt. Chem., t. xcv., p. 221. Zeitschrift für Chem., 1865, p. 599.
 - 7. STÆDELER and ARNDT. Chem. Centralblatt, 1864, p. 705.
 - 8. ABEL and MORLEY. Annal. der Chem. und Pharm., t. xciii., p. 311.
- 9. GIRARD and DE LAIRE. Moniteur Scientifique, t. ix., p. 245.
- 10. A. W. Hofmann. Moniteur Scientifique, 1872, p. 849.

Pseudotoluidine.

- 1. ROSENSTIEHL. Bulletin de la Soc. Indust. de Mulhouse, 1868, p. 543.
- 2. W. Korner. Compt. Rendus, t. Ixviii., p. 824.

Xylidine.

- 1. Church. Journ. für Prakt. Chemie, t. lxvii., p. 44.
- 2. DEUMELANDT. Zeitschrift fur Chem., 1866, p. 21.
- 3. C. A. Martius. Monatsbericht der Königl. Akademie der Wissenschaften zu Berlin, July, 15, 1869.

Industrial Preparation of Aniline.

- I. DEPOUILLY FRERES. Bulletin de la Soc. Indust. de Mulhouse, 1865, p. 200.
- 2. PERKIN. Moniteur Scientifique, 1865, p. 145.
- 3. BECHAMP. See Aniline.
- 4. KREMER. Dingl. Polytechn. Journ., t. clxix., p. 377.
- 5. VOHL. Dingl. Polytechn. Journ., t., clxvii., p. 437.
- 6. Brimmeyr. Dingl. Polytechn. Journ., t. clxxvi., p. 462; t. clxxix., p. 388.

Aniline Colours.

- 1. RUNGE. Annal. der Physik von Poggendorff, t. xxvi., pp. 67, 513.
- 2. A. W. HOFMANN. See Aniline; also, Compt. Rendus, t. xlvii., p. 472.

 Proceedings of the Royal Society, vol. ix., p. 284.
- 3. NATANSON. Annal. der Chem. und Pharm., t. xlviii., p. 297.
- 4. CRACE CALVERT. Journ. of the Society of Arts, June, 1858, p. 17.
- RENARD FRERES and FRANC. Brevet d'Invention, April 8, 1859, No. 40,
 p. 635, Five additions: Oct. 1, Nov. 19, Nov. 26, Dec. 17, 1859, and
 Feb. 14, 1860.

- 6. A. W. Hofmann. Comptes Rendus, t. liv., p. 418. Journ. für Prakt. Chem., t. lxxxvii., p. 226. Comptes Rendus, t. lvi., p. 1033. Zeitschrift für Chem., 1863, p. 393. Comptes Rendus, t. lviii., p. 1131. Journ. für Prakt. Chem., t. xciii., p. 208. Comptes Rendus, t. lvi., p. 945. Zeitschrift der Chem. und Pharm., 1863, p. 369. Comptes Rendus, t. lv., p. 817. Zeitschrift der Chem. und Pharm., 1863, p. 33.
- E. Kopp. Répert. de Chim. Appliq., t. vi., p. 257. Dingl. Polytechn. Journ., t. clxv., p. 382. Comptes Rendus, lii., 363.
- 8. Sopp. Brevet d'Invention, Feb. 19, 1866.
- g. GIRARD and DE LAIRE. Brevet d'Invention, Feb., 1867.
- TO. GIRARD, DE LAIRE, and CHAPOTAUT. Comptes Rendes, t. lxiii., p. 964; t. lxiv., p. 416. Traité des Dérivés de la Houille, p. 575.
- 11. LUTHRINGER. French Patent of Aug. 7, 1867.
- 12. Bolley. Schweiz. Polytechn. Zeitschrift, 1863.
- E. C. P. Ulrich. Brevet d'Invention, 1869. Moniteur Scientifique, 1869, p. 674.
- 14. COUPIER. Bulletin de la Soc. Industr. de Mulhouse, 1866, p. 259.
- 15. Schützenberger. Rapport sur les Procédés Coupier. Bulletin de la Soc. Indust. de Mulhouse, 1868, p. 925.
- 16. ROSENSTIEHL. Bulletin de la Soc. Industr. de Mulhouse, 1866, p. 264; 1871, p. 217, et Wagner's Jahresbericht, 1871, p. 764.
- A. W. HOFMANN. Rouge de Xylidine, Monatsbericht der Königl. Akademie der Wissenschaften zu Berlin, July 15, 1869.
- Safranin. Dingler's Polyt. Journ., t. ccii., p. 307. Bulletin de la Soc. Chim. de Paris, t., xvi., 1871, p. 383. Wagner's Jahresbericht, 1871, p. 772.
- 19. A. W. HOFMANN and A. GEYGER. Deutsche Chem. Gesellschaft, t. v., pp. 462, 526, 1870, Nos. 10, 11. Bulletin de la Soc. Chim. de Paris, t. xviii., 1872, p. 279.

Aniline Blue.

- GIRARD and DE LAIRE. Brevet d'Invention, July 6, 1860. Additions Jan. 2, 1861. Brevet du Jan. 2, 1861. Moniteur Scientifique, t. vii., p. 4. Traité des Dérivés de la Houille, pp. 585, 590.
- 2. Beissenhirz. Annal. der Chem. und Pharm., t. lxxxvii., p. 376.
- 3. FRITZCHE. Journ. für Prakt. Chem., t. xxviii., p. 202.
- 4. E. Kopp. Moniteur Scientifique, t. iii., p. 75. Brevet d'Invention, June 13, 1861.
- BECHAMP. Brevet d'Invention, June 22, 1860. Comptes Rendus, t. lii., p. 538.
- C. CALVERT, C. LOWE, and S. CLIFT. English Patent, June 11, 1860. Brevet Français, Déc. 12, 1860.
- 7. G. Schæffer and Gros-Renaud. Monit. Scientifique, t. iii., p. 293.
- 8. CH. LAUTH. Moniteur Scientifique, t. iii., p. 79.
- 9. Persoz, de Luynes, and Salvetat. Comptes Rendus, 1861, No. 14, p. 1010. Répertoire de Chim. Appliq., t. iii., pp. 131, 170.
- 10. Bécourt. Moniteur Scientifique, t. iv., Jan. 1, 1862.
- Monnet and Dury. Brevet d'Invention, May 30, 1852. Addition, Aug. 7, 1862. Addition, October 21, 1862.

- NICHOLSON. Moniteur Scientifique, t. vii., p. 5. Patent, July 10, 1862.
- 13. WILLIAMS. Repertory of Patent Inventions, March, 1864.
- 14. HOFMANN. Comptes Rendus, 1864, t. lix., p. 793.
- 15. COLLIN. Brevet d'Invention, May 16, 1862.
- 16. GIRARD, DE LAIRE, and CHAPOTAUT. Brevet d'Invention (GIRARD and DE LAIRE), March 21, 1866; Certificat d'Addition, March 16, 1867.
- 17. Bolley. Schweiz. Polytechn. Zeitschrift, 1863, p. 32.
- 18. Blumer-Zweifel. Moniteur Scientifique, 1869, p. 301.
- 19. E. WILLM. Bulletin de la Société Industrielle de Mulhouse, Nov., 1861.
- 20. J. Persoz. Brevet au nom de MM. Guinon, Marnas, et Bonnet, July, 1862.
- 21. RICHARD. Moniteur Scientifique, 1862, p. 463.
- 22. BULK. Deutsche Chem. Gesellschaft, t. v., p. 417; 1872, No. g. Bulletin de la Soc. Chim., t. xviii., 1872, p. 277.

Aniline Violet.

- 1. GIRARD and DE LAIRE. Brevet d'Invention, Jan. 2, 1861.
- 2. GIRARD and DE LAIRE. Brevet d'Invention, Feb. 21, 1867.
- 3. GIRARD and DE LAIRE. Brevet d'Invention, Feb. 25, 1867.
- 4. GIRARD and DE LAIRE. Traité des Dérivés de la Houille, p. 595.
- 5. E. C. Nicholson. English Patent, June 20, 1862.
- Delvaux. Brevet d'Invention, March 28, 1862. Certificat d'Addition, Oct. 10, 1862.
- 7. WISE. Le Technologiste, Aug., 1865.
- 8. Poirrier and Chappat. Brevet d'Invention, June 16, 1860. Certificat d'Addition du Aug. 11, 1866.
- 9. CH. LAUTH. Moniteur Scientifique, 1864, p. 336. Brevet d'Invention,
 December 1, 1866.
- 10. WANKLYN. Brevet d'Invention, Nov. 6, 1865.
- II. Perkin. Provisional English Patent, August 27, 1856; completed Feb. 2, 1858. Brevet Français, Feb. 20, 1858. English Patent, Sept. 10, 1864.
- 12. SCHEURER-KESTNER. Bulletin de la Soc. Industr. de Mulhouse, June, 1860.
- 13. A. SCHLUMBERGER. Bulletin de la Soc. Industr. de Mulhouse, March, 1862.
- 14. TABOURIN and FRANC. Brevet d'Invention, Aug. 6, 1858.
- 15. GREVILLE WILLIAMS. English Patent, April 30, 1859.
- 16. KAY. English Patent, May 9, 1859.
- 17. D. PRICE. English Patent, May 25, 1859; Brevet Français, Nov. 16, 1859.
- 18. Guigon. Brevet Français, May 30, 1861.
- 19. CH. LAUTH. Le Technologiste, Nov., 1861.
- 20. LEVINSTEIN. Brevet d'Invention, Sept. 2, 1864.
- 21. Bolley. Schweiz. Polytechn. Zeitschrift, 1858.
- 22. BEALE and KIRKHAM. English Patent, May 13, 1859.
- 23. DEPOUILLY et LAUTH. Brevet d'Invention, Jan. 19, 1860.
- R. SMITH. Provisional Protection, March 15, 1860. Final Specification, Aug. 17, 1860.

- 25. COBLENTZ, Brevet d'Invention, March 23, 1860.
- 26. J. Dale and H. Caro. English Patent, May 26, 1860.
- 27. G. PHILIPPS. Brevet d'Invention, Jan. 28, 1864.
- 28. Perkin. Annal. der Chemie und Pharm., t. cxxxi., p. 201. Patent 1864.
- 29. Bulk. See Aniline Blue.
- 30. A. W. Hofmann. Berichte der Deutsch. Chem. Gesellschaft, 6e année p. 263. Moniteur Scientifique, Mai, 1873.

Aniline Green.

- USEBE. Brevet d'Invention, Oct. 28, 1862. Note d'un Manusacturies. Moniteur Scientifique, vol. vi., p. 361.
- 2. Lucius. Polytechn. Centralblatt, 1864, pp. 1596, 1659.
- 3. LAUTH. Brevet d'Invention, December 28, 1865.
- 4. WANKLYN and PARAF. English Patent, Aug. 14, 1866.
- 5. KEISSER. Brevet d'Invention, April 18, 1866.
- A. W. Hofmann. Monatsbericht des Königl. Akademie der Wissenschaften zu Berlin, July 15, 1869.
- A. Poirrier, C. Bardy, and Ch. Lauth. Bulletin de la Société Chim. de Paris, t. xv., 1871, p. 156. Dingl. Polytechn. Journ., t. exeviii., p. 94. Wagner's Jahresbericht, 1870, p. 587.
- 8. GIRARD and DE LAIRE. Traité des Dérivés de Houille, p. 608.

Aniline Brown and Yellow.

- 1. H. KECHLIN. Bulletin de la Soc. Industr. de Mulhouse, Aug., 1865.
- 2. J. FAYOLLE. Brevet d'Invention, Nov. 15, 1864. Moniteur Scientifique, t. vii., p. 417.
- 3. GIRARD and DE LAIRE. Brevet d'Invention, March 23, 1863.
- 4. HUNT. Sillim. Amer. Journal, No. 1849.
- 5. A. W. HOFMANN. Annal. der Chem. und Pharm., t. lxxv., p. 356.
- 6. A. MATHIESSEN. Annal. der Chem. und Pharm., t. cviii., p. 212.
- 7. LUTHRINGER. Brevet d'Invention, Aug. 30, 1861.
- 8. MENÉ. Comptes Rendus, t. lii., p. 311.
- Q. A. SCHULTZ. Le Technologiste, Jan., 1866.
- 10. H. CARO and P. GRIESS. Zeitschrift für Chemie, t. x., p. 278.
- II. C. A. MARTIN and P. GRIESS. Zeitschrift für Chemie, t. ix., p. 132.
- 12. H. SCHIFF. Journ. der Chem. und Physik, 1864, p. 110. Le Technologiste, Oct., 1863.

Aniline Black and Grey.

- Lightfoot. Brevet d'Invention, Jan. 28, 1863, No. 57,192. English Patent, Jan. 17, 1863.
- 2. CORDILLOT. Moniteur Scientifique, t. vi., p. 569 (1864).
- 3. Ch. Lauth. Bulletin de la Soc. Chim. de Paris, Déc., 1864, Févr., 1866, May 20, 1873.
- 4. C. KECHLIN. Moniteur Scientifique, t. vii., p. 772.
- 5. Rosenstiehl. Bulletin de la Soc. Industr. de Mulhouse, 1865, Nov. et Déc., p. 436.

- 6. J. Persoz. Deutsche Industrie-Zeitung, 1868.
- 7. COUPIER. Brevet d'Invention, Sept. 17, 1867.
- 8. Castelhaz. Brevet d'Invention, Oct. 19, 1865, No. 69,083.
- g. C. Hartmann. Grothe's Muster-Zeitung, No. 33. Dingler's Journal, ccii., p. 389. Wagner's Jahresbericht, 1871, p. 761.
- 10. A. Müller. Chem. Centralblatt, 1871, p. 288. Wagner's Jahresbericht, 1871, p. 775.
- II. JARASSON and MULLER-PACK. Moniteur de la Teinture, Oct. 20, 1872. Bulletin de la Soc. Chim. de Paris, t., xix., 1873, p. 285.
- 12. J. Persoz. Moniteur Scientifique, 1872, p. 396.
- M. Vogel. Muster-Zeitung, 1868, No. 9. Becker und Reimann, Anilin-Färberei, Berlin, 1871, p. 26.

Naphthalin and its Derivatives.

- r. E. Kopp. Examen des Matières Colorantes Artificielles Dérivés du Goudron de Houille, Seconde partie, Couleur de Naphthaline. (Extrait du Moniteur Scientifique du Docteur Quesneville).
- Ballo. Das Naphtalin und seine Derivate in Beziehung auf Technik und Wissenschaft, Brunswick, 1870.
- 3. Th. Chateau. Couleurs d'Aniline, d'Acide Phénique, et de Naphthaline, Paris, 1868.
- BERTHELOT (Formation of Naphthaline). Will's Jahrb., 1866, p. 516, 1867, 1868.
- 5. VOHL (Préparation of Naphthaline). Dingl. Journ., t., clxxxvi., p. 138.
- 6. Kolbe (Constitution). Annal. der Chem. und Pharm., t. lxxvi,, p. 40.
- ERLENMEYER (Constitution). Annal. der Chem. und Pharm., t. cxxxvii., p. 346.
- 8. GRÆBE (Constitution). Annal. der Chem. und Pharm., t. cxlix., p. 25.
- 9. Faust and Saame (Chlorures de Naphtaline). Zeitschrift für Chem., 1869.
- 10. GLASER (Dérivés Bromés). Annal. des Chem. und Pharm., t. cxxxv., p. 40.
- II. Roussin (Nitronaphtaline). Comptes Rendus, t. lii. Dingl. Journ., t. clxi., p. 69.
- 12. NEWTON (Naphtaline Yellow). Patente, Dingl. Journ., t. clxxi., p. 72.
- 13. DUSART (Acide Nitroxynaphtalique). Comptes Rendus, t. lii., p. 1183, 1861. Journ. für Prakt. Chem., t. lxxxiv., p. 188.
- 14. E. KOPP (ib.). Répert. de Chim. Appliq., 1861, pp. 262, 306, 405.
- DARMSTADTER and WICHELHAUS (Binitronaphtaline). Berl. Bericht, 1869, p. 274.
- 16. LAURENT (ib.). Annal. de Chim. et de Phys., t. lix., p. 381.
- 17. TROOST (ib.). Bullet. de la Soc. Chim. de Paris, 1861, p. 74.
- 18. Roussin (Naphtazarine). Comptes Rendus, t. lii., p. 1034.
- 19. LIEBERMANN (ib.). Berl. Ber., 1870, p. 905.
- 20. AGUIAR and BAEYER (ib.). Berl. Ber., 1871, pp. 251, 301, 438.
- CAREV LEA (Réduction of Binitronaphtaline). Dingl. Journ., t. clxvi., pp. 317, 237.
- 22. TROOST (ib.). Bulletin de la Soc. Chimique de Paris, 1861, p. 74.
- 23. MÜLHAUSER (ib.). Annal. der Chem. und Pharm., t. cxli., p. 240. Will's Jahrb., 1865, p. 528, 1866, p. 619.

- 24. ZININ (Naphtylamine). Annal. der Chem. und Pharm., t. xliv., p. 283.
- 25. CAREY LEA (ib.). Dingl. Journ., t. cxvi., p. 237; t. clxxiii., p. 480; t. cxc., p. 428.
- 26. Piria (Naphtazarine). Annal. der Chem. und. Pharm., t. lxxviii., p. 62; t. ci., p. 92.
- SCHEURER-KESTNER and RICHARD (Violet de Naphtylamine). Dingl. Journ., t. clxii., pp. 295, 193.
- 28. CLAVEL (Rouge de Naphtylamine). Dingl. Journ., t. cxl., p. 428.
- 29. CHURCH and PERKIN (Nitrosonaphtyline). Chem. Centralblatt, 1856, p. 604; 1863, p. 913.
- 30. MARTIUS (Jaune de Martius). Dingl. Journ., t. clxxxvii., p. 165.
- 31. WICHELHAUS and DARMSTADTER (ib.). Berl. Ber. 1869, p. 113.
- 32. E. VON SOMMARUGA (Indophane). Deutsche Chemische Gesellschaft, t. iv., p. 94, 1871. Bulletin de la Soc. Chim., 1871, t. xxv., p. 281. Wagner's Jahresbericht, 1871, p. 750.
- 33. Hofmann (Rouge de Naphtaline). Berl. Ber., 1869, pp. 374, 412. Dingl. Journ. t. cxlii., p. 513.
- 34. Zinin (Naphtalidam). Journ. für Prakt. Chem., t. xxxvii., p. 29; t. lvii., p. 173.
- 35. D'AGUIAR (ib.). Berl. Ber., 1870, p. 27.
- 36. GREBE (Naphtoquinones). Annal. der Chem. und Pharm., t. cli., p. 1.
 Berl. Ber., 1869, p. 612.
- 37. DEPOUILLY (Acide Chloroxynaphtalique). Bulletin de la Soc. Chim., 1865, p. 10.
- 38. MERZ (Acide Sulfonaphtalique). Zeitschrift für Chem., 1868, pp. 34, 393.
- 39. MERZ and MULHAUSER (Cyannaphtaline). Zeitschrift für Chem., 1869,
- 40. WICHELHAUS and DARMSTADTER (ib.). Berl. Ber., 1869, p. 356.
- 41. GRIEFF (Naphtol). Chem. Centralblatt, 1863, p. 125.
- 42. Schaffer (ib.). Berl. Ber., 1869, p. 90. Zeitschrift für Chem., 1869,
- 43. LAURENT (Acide Phtalique). Revue Scientifique, t. xiv., p. 560.
- 44. VOHL (ib.). Annal. des Chem. und Pharm., t. oxliv., p. 71.

Anthracen and its Derivatives.

- E. Kopp (Sur l'Anthracène et ses Dérivés). Moniteur Scientifique, 1869,
 t. xi., pp. 465, 851, 873, 1065, 1138; 1870,
 t. xii., pp. 753; 1871,
 t. xiii.,
 pp. 531, 691; 1872,
 t. xiv., pp. 33, 252, 319, 681; 1873,
 t. xv., p. 14.
- 2. G. AUERBACH. Das Anthracen und seine Derivate. Berlin, 1873.
- 3. Dumas and Laurent (Paranaphtaline). Annal. de Chim. et de Phys.., troisième série, t. l., p. 187.
- 4. LAURENT (Anthracène). Annal. de Chim. et de Phys., troisième série, t. lx., p. 230; t. lxvi., p. 148; t. lxxii., p. 415.
- FRITZSCHE (ib.). Journ. für Prakt. Chem., t. 1xxiii., p. 282; t. cv., p. 129.
 Rep. Chim. Prat., 1862, t. iv., p. 269. Bulletin de la Soc. Chim., t. vi., p. 474; t. viii., p. 191; t. xii., p. 414.
- Anderson (Anthracene and its Derivatives). Annal. der Chem. und Pharm...
 cxxii., p. 294.

- BERTHELOT (Formation de l'Anthracène). Bulletin de la Soc. Chim., t. vi., pp. 268, 272, 280; t. vii., pp. 43, 224, 274, 279, 288; t. viii., pp. 195, 225, 231; t. ix., p. 295; t. x., p. 483.
- GRÆBE and LIEBERMANN (Anthracene and its Derivatives). Annal. der Chem, und Pharm., 1870, t. vii. (Supplément), p. 257. Berl. Ber., 1870, pp. 634, 637. Bulletin de la Soc. Chim. t. xi., pp. 178, 271, 516.
- Q. LIEBERMANN (Anthraquinone). Berl. Ber. 1871, pp. 109, 230.
- IO. GREIFF (Préparation de l'Anthracène). Dingl. Journ., t. cxciii., p. 511; t. cxciv., p. 351.
- 11. GESSERT (ib.). Polytechn. Notizbl., 1870, p. 221.
- 12. SCHULLER (ib.). Berl. Ber., 1870, p. 548.
- 13. WARTHA (Anthraquinone). Berl. Ber., 1870, p. 548.
- 14. Bolley (Nitroanthracène). Berl. Ber., 1871, p. 671.
- ,, (Alizarine). Schweiz, Polytechn. Zeitschrift, 1869, p. 145;
 1870, pp. 31, 51.
- 16. PERKIN (Derivatives of Anthracene and Anthraflavine). Chemical News, vol. xxi., pp. 116, 139; vol. xxii., pp. 37, 283; vol. xxiv., p. 226. Journal of the Chemical Society (3), t. viii., p. 133; t. ix., p. 25.
- 17. BÖTTGER and PETERSEN (Dérivés de l'Anthraquinone). Berl. Ber., 1871, pp. 226, 301.
- 18. BÖTTGER (Orange d'Anthracène). Polytechn. Notizblatt, 1870, p. 225.
- 10. Roscoe (Alizarin). Chemical News, 1870, vol. xxi., p. 185.
- 20. Dale and Schorlemmer (Alizarine). Berl. Ber., 1870, p. 838.
- 21. SCHUNCK (Anthraflavine). Berl. Ber., 1871, p. 359.
- 22. STRECKER (Nitroxyalizarine). Zeitschrift für Chem., t. iv., 1868, p. 263.
- LIMPRICHT (Formation de l'Anthracène). Bulletin de la Soc. Chim., t. vi., p. 467.
- 24. AUERBACH (Isopurpurine). Moniteur Scientifique, Aug. 1872, p. 686.

 Das Anthracen und seine Derivate, Berlin, 1873, p. 122.
- W. H. PERKIN (Anthrapurpurine). Bulletin de la Soc. Chim., t. xviii., 1872, p. 527; t. xix., 1873, p. 519. Moniteur Scientifique, September, 1873, p. 788.
- H. GROTHE (Printing with Alizarine). Grothe's Muster-Zeitung, 1871,
 No. 21, p. 142; No. 30, p. 242; No. 46, p. 362.

Colours Derived from Phenol.

- DALE and SCHORLEMMER (Rosolic Acid). Berl. Ber., 1871, pp. 231, 968.
 Bulletin de la Soc. Chim., 1871, t. xvi., p. 374. Chemical News, vol. xxvii., p. 103. Bulletin de la Soc. Chim., September 20, 1873.
- 2. H. Fresenius (ib.) Journ. für Prakt. Chem. t. iii., p. 477. Bulletin de la Soc. Chim., 1871, t. xvi., p. 375.
- BAEYER (Colours derived from Phenols). Berl. Ber., 1871, pp. 457, 555.
 Bulletin de la Soc. Chim., t. xvi., 1871, pp. 184, 377.
- 4. F. GRIMM (Phtaléine de l'Hydroquinone et Quinizarine). Deutsche Chemische Gesellschaft, t. vi., p. 506, 1873. Bulletin de la Soc. Chim., Octobre 5, 1873.
- WESELSKY (Nitro-Derivatives of Resorcin). Berl. Ber., 1871, p. 613.
 Bulletin de la Soc. Chim., 1871, t. xvi., p. 186.

Cyanin.

- 1. Runge (Leucoline). Poggend. Annal. der Phys., t. xxxi., p. 68.
- 2. HOFMANN (ib.). Annal. der Chem. und Pharm., t. xlviii., p. 27.
- 3. GERHARDT (Chinoline). Revue Scientifique, t. x., p. 186.
- 4. GREVILLE-WILLIAMS (Chinoline Blue). Chemical News, vol. ii., 1860. p. 219.
- 5. HOFMANN (Cyanine). Dingl. Polytechn. Journ., 168, p. 125. Comptes Rendus, t. lv., p. 84.
- 6. SCHNITZER (ib.). Chem Centralb., 1861, p. 636.
- 7. NADLER and MERZ (ib.). Journ. für Prakt. Chem., t. c., p. 129.
- 8. Schönbein (ib.). Journ. für Prakt. Chem., t. cv., pp. 385, 449.
- 9. HORACE KÖCHLIN (Cinchonine). Répertoire de Chim. Appliq., 1861, t. iii.. p. 381.
- Io. H. Köchlin (Dalleïochine). Bulletin de la Soc. Industrielle de Mulhouse, 1860, t. xxx., p. 458.

Colours Derived from Aloes.

- I. Schunck (Acide Chrysamique). Annal. der Chem. und Pharm., t. xxxix., p. 1; t. lxv., p. 235.
- 2. Mulder (ib.). Annal. des Chem. und Pharm., t. lxviii., p. 329; t. lxxii..
- 3. LAURENT (ib.). Compte Rendu des Travaux de Chimie, 1850, p. 163.
- 4. C. ROBIQUET (Aloès et Derivès). Annual. des Chem. und Pharm., t. lx.,
- 5. Sacc (Dyeing with Derivatives of Aloes). Dingl. Journ., t. cxxxiv..
- 6. BOUTIN (ib.). Le Teinturier, p. 355.
- 7. LINDNER (ib.). Dingl. Journ., t. CXXXV., p. 312.
- 8. Löwe (ib.). Dingl. Journ. t. cxxxvii., p. 238.
- 9. STENHOUSE and MÜLLER (Chrysammic Acid). Zeitschrift für Chem., 1866, p. 565.
- 10. Finck (Acide Chrysocyamique). Zeitschrift für Chem., 1865, p. 519.
- II. TILDEN (Chrysammic Acid and Aloïn). Chemical News, 1872, t. xxv., pp. 229, 244.

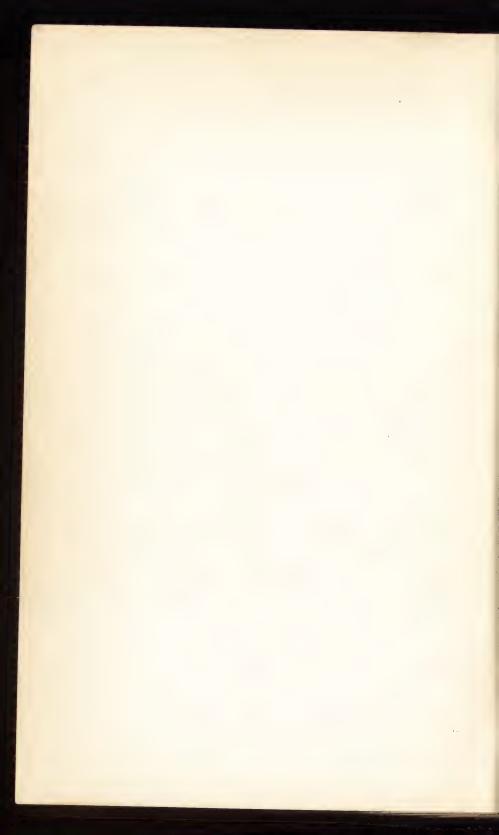
Rufigallic Acid.

- 1. Löwe (Acide Rufigallique). Journ. für Prakt. Chem., t. cvii., p. 296.
- 2. Malin (ib.). Annal. der Chem. und Pharm., t. cxxxi., p. 345.
- 3. JAFFE (ib.) Berl. Ber., 1870, p. 694.
- Hugo Schiff (ib. et Acide Tannique). Berl. Ber., 1871, pp. 231, 968.
 Bulletin de la Scc. Chim., 1871, t. xvi., p. 198.

Murexide.

- I. PROUT (Purpuric Acid). Annal. of Philos., vol. xiv., p. 363.
- 2. Liebig and Wöhler (Murexide). Annal. des Chem. und Pharm., t. xxvi., p. 319.

- 3. Braun (Préparation de l'Acide Urique). Dingl. Journ. t. clii., p. 191.
- BROOMAN (ib. et Murexide). Dingl. Journ., t. exliv., p. 68; t. cxlv., p. 137;
 t. clvi., p. 236.
- SCHLUMBERGER and DOLLFUSS (Teinture avec la Murexide). Bulletin de la Soc. Industrielle de Mulhouse, 1854, No. 120, pp. 242, 280.
- 6. Depoullly and CH. Lauth (ib.). Moniteur Scientifique, 1859, p. 968.
- 7. E. Kopp (Murexide). Répertoire de Chim. Appliq., 1859, t. i., p. 79.
- 8. CLARK (ib.). Dingl. Polytechn. Journ., t. cli., pp. 141, 203.
- 9. TH. WURTZ (Teinture). Dingl. Journ. t. cliii., p. 212.



INDEX.

Acid, purpuric, 168

ACETATE of lime, red liquor from, 289 Aceto-ferruginous solutions, application of, 290 Acid, aloetic, 417 - amalic, 509 - anthrachinon bisulphuric, 224 - anthranilic, 172 - carbolic, 215 - carminic, 356 - carthamic, 142, 385 - catechutannic, 491 - chlorostannic, 530 - chloroxynaphthalic, 679 - chrysammic, 417 - chryseic, 678 - chrysinic, 426 - chrysophanic, 425 - erythric, 370 - erythrosic, 364 - from cotton, 36 - gallic, 502 - gentianic, 426 - hydrochloric, 520 - isopurpuric, 219, 674 - lizaric, 242 — morintannic, 40б - muriatic, 520 - nitric, 74, 520 - nitrococcussic, 357 - nitrocuminic, 512 - nitro-xynaphthalic of Dusart and Gelis, 678 - normal hydrochloric, 124 — — nitric, 124 — — oxalic, 124 - - sulphuric, 122 - orsellic or orsellinic, 373

- parelline or parellic, 374

Acid, preparation of picric, 673

- phenic, 215

picric, 219

- picramic, 219

- picrocyanic, 219

- pyrogallic, 503

- quercitannic, 396 - rosalic, 674 - rosolic, 683 - rufigallic, 687 - rutinic or rutic, 410 - stannic, 519 - sulphindigotic, 445 - sulphonaphtholic, 681 - sulphuric, 521 - tannic, 502 - tartaric, 549 - usnic, 425 - viridic, 513 - vulpic, 425 Acidimetry, 131 Ageing, 280 Albumen, 75 - adulteration of, 688 - blood, 639 - coagulated, 76 - egg, 80 - qualitative testing of, 78 - quantitative estimation of, 78 - substitutes, 81 - vegetable, 75 Albumenoid substances, 73 - applying in fixing colours, 80 Alcohol, phenic, 215 - substances soluble in, 234 Alcohols, naphthylic, 680 Aldehyde, green, 205 Algaroth, 509 Alizarin, 143, 242, 252, 308 — artificial, 222 - green, 246, 248. - pure crystalline, to dye with, 247 - yellow, 246 Alkalies, carbonated, 125 - caustic, 129 - estimation of, 128 Alkalimeter, 123

Alkalimetry, 122

Alkanet, 384

Alloxan, 169 Alloxantine, 169 Aloe resin, 415 Aloes, 415 - varieties of, 415 Aloetic acid, 417 Aloetin, 416 Aloin, 416 Alum, 275 - ammonia, 275 - neutral or cubical, 276 - potash, 275 Alumina, 143 - acetate of, 142, 207, 226 - fixing upon woven fabrics, 279 - hyposulphite of, as a mordant, 285 - hydrochlorate of, 276 - muriate of, 276 - nitrate of, 226, 276 - sulphate of, 276 Aluminate of potassa, 27 Amalic acid, 509 Ammonia, 120, 130 - carbonate of, 121 - hæmatate of, 345 — isopurpurate of, 219 — nitrate of, 121 Ammoniacal cochineal, 358 - salts, 120 Ammonium, chloride of, 121 - chlorostannite of, 526 Amylum, 66 Aniline black, with madder-red and

chrome-orange, specimen, 647

— blue, apparatus for preparation of, 198

— colouring linen yarn, 61

— method of manufacturing, M.

method of manufacturing, M
 MARNAS'S, 196
 colours derived from, 171

— detection of, 669
— method of fixing upon cotton, 195
— crimson, 187

discovery of, 171HOFMANN'S process, 173

— HOFMANN'S process, 173 — mordants, 185

- red, 178

- production of, 178
- salt, solution of, 645

Anilines, commercial value of, 176 Animal fibres, 73

- origin, thickenings of, 73

Annatto, 426
— colouring matters of, 427

Anotto, 426 Anthokirrin, 509 Anthracen, 222 — colours, 222

- method of determining, 690

- orange, 681

- quantitative examination of, 695

Anthrapurpurin, 683 - discovery of, 327 Apparatus, padding, 582 Application colours, 635 Aquafortis, 521 - single, 521 Arabine, 70 Archil, see Orchil. Argentine, 151 Argol, red, 549 -- white, 549 Argols, 548 Arsenic and glycerin standard, 207 - and arsenious acid, 11 - mordants, 545 - preparation of, 223 Artificial alizarin, printing with, 225 Astragalus verus, 71 Astringents, 490 - true, 499 Aurin, 683 Avivage, 275, 301, 352 Azaleine, preparation of, 179

BABLAH, 509

Azuline, 196

Babulah, 509
Babulah, 509
Ball soda, 114
Baphia nitida, 341
Balsamodendron, 382
Baraniline, 176
Barbatimas, 509
Bark, alder, 508
— barberry, 423
— butternut, 510
— mahogany tree, 512
— Panama, 652
— pomegranate root, 512

— quercitron, 394
BARLOW, Mr., bleaching under pressure, 45

Barwood, 341
— red, 341
Baryta, sulphate of, 151
Bath, arsenite of soda, 157

- chalk, 325
Batist. Flemish, 57
Bauxite, 279

Bearberry, 509
BENTLY, DAVID, continuous process

of bleaching, 52
Benzol, chloride of, 245
— discovery of, 173
Benzyl, chloride of, 674
Berberine, 423
Berries, Persian, 403
— privet, 512
Bichloride, aqueous, 530
Bichrome olive, 96

Bignonia chica, 388

Bilberries, 509 Binitro-anthraquinon, 682 Bismarck, 98 - aniline, 98 -- colouring linen yarn, 62 -- for woollen yarn, 629 Bisulphate of potash, III Bixin, 141, 426 Black, 99, 624, 630, 635, 639, 692
— aniline, 211, 646 -- specimen, 215 - blotch, 624 - bluish application, 347 - cheap, 100 - chrome, 99 - colouring linen yarn, 62 - fast, 100 - for French merinos, 624 for objects, 624for silk-striped thibets, 100 - madder and aniline, specimen, 579 - sumach, 100 — on woollen yarn, 629 Blacks, to test, 662 Bleaching, 44, 275
— continuous process of, 52 - carpet yarn, 88 — field, 312 — linen, 57 — liquor, Ramsay's, 139 — Wilson's, 139 - powder, 139 - silk, 106 -- under pressure, 45 - wool, 86 - woollen yarn, 88 Bleu de Lyons, 196
— de Mulhouse, 196 - de Paris, 196 Blue, 338, 631, 635 - aniline, 92 - chrome, 91 - colouring substances, 438 - dark, 625 — — indigo, 91 — — specimen, 164 - French, 167 - iron, 201, 463 - light, specimen, 164 - naphthoic, 679 - Nicholson's, specimen, 203 - Prussian, 91, 162 - purple, 91 - royal, 625 - Runge's, 190

— Saxony, 91 — topped logwood, 90

- resist for, 485, 593

- Turnbull's, 165 Blues, China, 565

-- cobalt, 167

Blues, detection of, 663 - refined, 198 - soluble, 199 Bluish-black application, 347 Boiler incrustations, 14 Bombyx, 104 Bowking, 48 Branning, 309 Brauna-wood, 510 Bresiline, 335 Broadcloth, dark blue for, 90 Bromelia ananus, 64 Bronzes, 566 - manganese, 638 Brown, 227, 626, 632, 636 - camwood, 97 - chrome, 97 - fast, 97 - light, 97 - naphtha, 208 - standard dark, specimen, 604 - - light, specimen, 604 Browns, aniline, 207 Buccinum, 171 Buff, 626 Buckwheat, colouring matter from, 412 Burls, 539 - chemical removal of from wool and woollen goods, 694 ACTACEÆ, 350 Cactin, 510 Cadmium, sulphide of, 154

Cæsalpinia brasiliensis, 331 — crista, 331 - echinata, 331 — sappan, 332 — vesicaria, 332 Calico, Hofmann's violet on, 613 - printing aniline colours on, 689 Calico-printing, styles of, 563
— printing-ink for use in, 688 Campeachy, 342 Cannabis sativa, 63 Cane-sugar, 233 Caoutchouc, solution of, 639 Caragara, 388 Carbonaceous grey, with chromeblack, chrome-green, chrome-yellow, and extract of madder, specimen, 643 Carbonate of ammonia, 121 - of lime, 150

— of soda, 113 Carbonated alkalies, 125 Carminaphtha, 679 Carminates, chemical history of, 357 Carmine, 359 - adulteration of, 359

- prescriptions for preparation of, 359

Carmine-lake, 360 Carminic acid, 356

Carpet yarn, bleaching, 88

Carpets, colouring linen yarn for, on the small scale, 58

Carotin, 424

Carrot roots, yellow colouring matter of, 424

Carthamin, 385, 386

Carthamus tinctorius, 384

Casein, 78, 185 Cashew, 490 Catechu, 490, 493

Catechuin, 492 Catechutannic acid, 491

Caustic alkalies, 129 Cellulose, 17, 19

Cerise, 675 Chalk, 150

- French, 151

Charbon sulphurique, 247, 257

Chayaver, 328 Chemical ag agents, bleaching with other, 56

Chemick, 49 Chestnut, 510 Chica, 388

Chicory, 510 Chinese yellow dyes, 421

Chlorate of potash, 113 Chloride of ammonium, 121

- of benzol, 245 - ferric, 536

- ferrous, 536 - of lime, 120, 138

- of manganese settlers, 133

- of sodium, 119 - stannic, 530 Chlorides, 132 Chlorimetry, 132

Chlorine, 132 - in chlorine water, estimation of, 140 - introduction of, of Messrs. Blech,

STEINBACH, and MANTZ, 311 - method, WELDON's, 132

- preparing, 132 - water, 132

Chloring, 310 Chlorogenin, 234 Chlorophyl, 435

Chocolate, 626, 632, 636

Chromate colours, use of, M. LAS-SAINGER, 154

- of potash, III Chrome alum, 544

- or canary yellow, specimen, 155

- green, 156 - specimen, 157

- orange, light and dark, specimen,

Chromium, metaphosphate of, 158

Chromule, 435

Chrysammic acid, 417 Chrysammid, 687

Chrysaniline, 209 Chrysinic acid, 426 Chrysophanic acid, 425

Chrysoretin, 510 Chrysotoluidine, 183, 210

Cinnabar, 152 Citrates, 234

Cloth, dunging of, for garancin work.

Coal-tar, 173 Coccus, 350 - Cacti, I

Coccedia viridis, 510 Cochineal, 1, 350, 609

- ammoniacal, 358 - cultivation of, 352

- employment of in dyeing and printing, 361

- Honduras, 352 - Java, 353 - oak, 353

- paste, 88 - selection of, 361

- shades obtainable upon wool by means of, 363

- Vera Cruz, 352 Cocoa-nut tree, 510

Coir, 64 Cold water, substances soluble in, 233

Colour bath, 247 - cochineal, detection of, 670

— stone, 99 — wood, 380

Colours, aniline, DALE's process for printing and dyeing with, 692

- anthracen, 222 - application, 635

- behaviour of, on different fibres. with reagents, 669

- cyanogen, 162 - fixing of, 80, 144

- from uric acid, 168

— garancin, 564, 579 — influence of light upon, 655 - madder, 564

- detection of, 671 -- naphthalin, 220

- on woollens, 89 - on wools and warps, 100

- pigment, 566 - soluble in water, 252

- spirit, 565, 635

- steam, 565, 598 - upon calico, red and rose-reds used

for, 338 — yellow vegetable, 393 Colouring matters, 252 - - brown and black, 490 Colouring matters, green, 428

- — in cotton, 37, 39 - — new class of, 690

- of doubtful existence, 252 - of organic origin, 168

— — of various origin, 388

-- valuation of quantity in madder, 272

- yellow, of Chinese origin, 421 COOK, JAMES, singeing cotton fabric, 44

Copper, acetate of, 545

— aceto-arsenite of, 156

- ammoniuret of, 546 - arsenite of, 156

- chloride of, 547

- muriate of, 547

nitrate of, 547sulphate of, 547 Copperas, 535

Corallin, 696 - orange-red, 633

- preparation of, 217 - yellow, 683

Corchorus olitorius, 63

Cork, 518 Cotton, 21

- acid from, 36

-bleaching raw, in small quantities, 52

- cochineal-red on, 689 - colouring matters in, 37, 39

- fibre, 21

- constituents of, 29 - steam black on, 347

- stockings, bleaching, 50 - warps, dark spirit violet on, 692

- - aniline blue, magenta, purple, Saxon blue, scarlet on, 101

- wax, 30, 34

- yarn, dyeing aniline blacks on, 688

Cow-dung, 294

influence of in cleansing, 296

Crabbing, 654

Crajura, 388 Creeper, Virginia, 513 Crimson, colouring linen yarn, 60

- with cochineal, 93

Crocin, 423 CRUM, WALTER, cotton, 28

Cuba wood, 365 Cudbear, 368

- adulteration of, 378 - manufacture of, 377

Curcumin, 418

- researches on, by M. F. W. DAUBE,

Cutch, 490

- brown (fast), colouring linen yarn, 62

- fixing by means of bichromate (MM. KŒCHLIN Frères), 496

- yellow, 491 Cyanin, 390, 685 Cyanogen colours, 162

ALLEIOCHIN, 686

Dahlia, 94 Decomposed vat, 90

Delaine, preparing, 615 Delaines, method of printing, 613

Dextrine, 68

Discharge, 317 - style, 594

— white, 692 Diphenylamine, 675

Divi-divi, 500 Drab, 98

Dung, substitutes for, 297

Dung-bath, 297 Dye-beck, 299

Dye-lac, 355 Dye materials, 142

Dyewoods, preparation of extracts of,

Dyes, Chinese yellow, 421

- detection of on yarn or pieces, 662 Dyeing, green, 432

- operations accessory to, 651 - Turkey-red, 321

- use of Epsom Salts in, 689

EAUX de Javelle, 139, 314

Eaux de Labarraque, 139

Ebony green, 511 Effects, indigo, 585 Egg albumen, 80

Enlevage, 317 Epidermic products, 82 Erythric acid, 370

Erythrite synonyms, 371

Erythrine, 370 Erythrodanon, 228 Erythrose, 364

Erythrozym, 239 Extract of madder red and pink with chrome orange, green, ultra-marine blue, and chrome black (specimen), 644

FECULA, 68

Feuille Morte, 380 Fibre, cocoa-nut, 64

- linen,

— vegetable, 17, 183 Fibres, animal, 73

- cotton, 21

- mineral, 16

 vegetable, distinguishing from each other, 65

- woollen, 83 Fibrine, 78

Fibroine, 105 Finishing, 655 Firing, 529

Flax, 27, 57

New Zealand, or Phormium tenax, 64, 107

- to distinguish from ordinary flax or hemp, 65

- ordinary, to distinguish from New Zealand flax, 65

Fleur de garance, 253, 271

Flowers, colouring matters of, 389, 424

Fustet, 411 Fustic, 405, 349

- carmine, 365

- colouring matters of, 405

— detection of, 672

- old, 405

- varieties of, 405

young, 411Zante, 411

Fustin, 411

GALLS, Aleppo or Turkey, 499

- chief commercial varieties, 499

- French, 499

- Istria, 499

- Morea, 499

- Piedmontese, 499

— so-called Marmorine, 499 — Smyrna, 499

Gallein, 568, 684

Gambier, 490

Garance, 228 Garançage, 275, 300 Garanceux, 253, 261

Garancin, 257
— dunging of cloth for, 299

— specimen, 579 — substitute for, 262

- red mordant for, 284

- style, 308

Garnet, soluble, 219 Gelatin, solution of, 502

Gentianic acid, 426

Geranosine, 206

Glucose, 233 Glucosides, 240, 252

Gluten, 78

Goods, woollen, printing, 624

Gossypium arboreum, 21

Grain, Polish, 356 Grass, Chinese, 63

Green, 627, 633, 636, 638

— aniline, 96, 202

-- with picric acid, 96

- Arnaudon, 158

- Barasat, 435

- Chinese, 428

- chrome, 95

Green, colouring linen yarn, 59

crystalline, 205dyes, of vegetable origin, 434

- for broadcloth, 95

- for yarn, 95 - iodine, 202

- manufacture of, 202

- logwood, 95

- methylaniline, 678

- olive, 96

- padded ground, with design in madder, red and pink, chrome-orange, green and black, specimen, 645

- Paris, 678

— Plessy, 158 — quinine, 686

- Scheele's, 156

- Schweinfurt, 156

- soluble, preparation of, 204

- Wilner, an arsenical, specimen, 157

Greens, detection of, 666

- dipped, 594

- indigo, 591 Grey, 628, 633

- aniline (CASTELHAZ), specimen,

680

-- silver, 99

Greys, aniline. 210

Guano, Peruvian, 169 Guigner's green and chrome-green, chrome-black and dichromate of

lead, specimen, 641

Guilandina, 329

Gum, 69, 233

— Arabic, 70 — kino, 491

- lac, 353 - Senegal, 70, 286

- tragacanth, 71

— yellow, 673

Gums, soluble in water, belonging to the species of Arabic gums, 69

Gypsum, 150

HACHROUT, 330

Hæmatin, 345 Hæmatoxylin, 343 Hæmatoxylon campechianum, 342

Harmala red, 364

Heath, 511 Hellebore, 511

Hemlock, 511

Нетр, бз

- Bombay, 64

- Manilla, 64

Ramee, 63

- Rhea, 63

Hibiscus cannabinus, 64

Hiccory, 511

Hoang-pé-pi, 421 Hoang-tchi, 422 Hohang-teng, 421 Holly, 511 Hollyhock, 511 Homorceine, 219 Horse-chestnut, 511 Horse-radish, 511 Hosiery, indigo-blue on wool, 90 Hydroquinon, derivatives of, 684 Hydroxide of sodium, 129 Hypernic, 60 Hypochlorite of lime, 120 - of potash, 113 -- of soda, 119 Evpouhlorites, estimation of, 141

INDIAN yellow, 425

Hyposulphite of soda, 119

Incigo, 89

- adulteration of, 462

- blue, composition of materials used for discharging, 475 - - part logwood, 91

- blues, 565

- bottom, mode with, 98

- Brazil, 457

- Caraccas, 456 - carmine, 463

- Carolina, 457 - detection of, 672 -- green, 435

- Guateir ala, 456

- impurit es found in, 462

- industrially-prepared sulphuric acid derivatives of, 463

- Madras, 456 - Manilla, 456

- manufacture of in Bengal, 447 -- Mexican, 456

- mode without, 98

- printing with, 475 - receipts for dissolving, 463

- reduction of, 469 -- refined, 466

- sulphuric derivatives of, application of, 487 -- preparations of, used in dyeing

and printing, 465 - trade terms generally applied to, 457

-- vats, theory of, 469 -- white, 441

Indigos, Oude and Coromandel, 455 - Senegal and Mauritius, 457

Indigotin, 142, 438, 443

- amorphous, 439

fixing, by reduction method, 468
methods for quantitative estimation of, 458

-- of fixing in printing, 482

Indigotin, sublimed, 439

- to bleach, 458 Indin, 447

Indirubin, 454

Insoluble colours, mechanical fixation

Introduction, 1 Iodine, 140 - green, 202 - solution of, 523 Iron, acetate of, 536

- black, 538 - blue, 538

- buff, 154 - - specimen, 155

- common, for drabs, 539 - hyposulphite of, 292

- in water, 11, 12

- liquor, 291 - muriate of, 536 - nitrate of, 61, 536

permuriate of, 536persulphate of, 536

- protosulphate of, 535 - red sulphate of, 536

- solution of protochloride of, 536

- to fix peroxide of, 290 Irons, burling, 539 - saddening, 539 - to test, 540 Isatin, 446 Isatis indigotica, 454

- tinctoria, 452 Isopurpuric acid, 219, 674

Isopurpurin, artificial, 682 ASPEADA, 351

Jaune d'Or, 222

Job dyeing, 653 Jute, 63

KERMES, animal or vegetable, 352

Khail cedra, 511 Kiers, bleaching, 45 Kino, 491 Krapp, 228 Knoppern, 499

Kuphaniline, 176 Kyanol, 17:

AC dye, 355

- - colouring matter of, 355

- · lake, 355 Lactarine, 79, 185

Lake colours, preparation of, 365

- green, 366 Lakes, 337 - aniline, 367 Lakes, blue, 366

cochineal, 366yellow and orange, 367

Lamium album, 511 - purpureum, 511

Lan, 489 Lapathin, 426

Lapis lazuli, 80, 158

Lavender, 99 Lawsonia inermis, 511 Lazulite, white, 589 Lead, acetate of, 541

- alkaline solutions of, 541

- nitrate of, 541 - subacetate of, 541 - sugar of, 541

- sulphate of, 541

Leaves and green parts of plants, colouring matters of, 435

LEBLANC'S process, 117

Legumine, 79

Leguminosæ, 337, 342 Libavius, fuming spirit of, 530

Libi-divi, 500

Lichens, chemical history of colouring matters of, 369

- colouring matters derived from, 367 - discovery of colour-yielding pro-

perties of, 367 - yellow colouring matters of, 425 Light, action of as a destroyer of colours, 657

- experiments on action of, 659

Lilac, 628

- colouring linen yarn, 61

- standard, 603 Lilacs, steam, 608 Lime, acetate of, 227

- action of, for fixing purples, 320

- carbonate of, 150

- chloride of, 49, 120, 138, 311

- hypochlorite of, 120

- in water, 11 - salts, 120

- sulphate of, 150 Linen, bleaching, 57

- fibre, 57

- yarn for carpets, colouring, 58

- white bleaching, 58 Linum usitatissimum, 57 Liquor, black, 536, 649

- iron, 291

potassa, 314red, 288

Liquors, red, prescriptions for, M. D.

KŒCHLIN, 283 Lithospermum arvense, 511

Litmus, 383

- chief use of, 380 Livi-divi, 500

Lixiviation, SHANKS'S process, 115

Lizaric acid, 242

Logwood, 342 blue, 346decoctions, 348

- extract of, 347

Lokao, 428

- French process for dyeing with

- purification of, 430 Lutein, 393

Luteolin, 407 Lye, crude soda, 116

ACHINE, cylinder, 551

- perrotine, 551

- printing, routine of, 560

- straining (Dollfus and Mieg), 562 Maclurin, 407

Madder, 228, 290

- adulteration of, 232, 273

- application of colouring principles contained in, 315

- art of dyeing with, 300

- commercial products or derivatives from, 252

- composition of, 233 - concentration of, 257

— conspectus of colours of, 252 — cultivation of, 230

- dyeing with, 299

- lake, 365

- lakes, preparation of, 269

- - of deepest shade, 366 - orange, 252

ordinary, style work, 307preparations for dyeing purposes,

- preparing bloom of, 254 - printing, 315

process of purifying, 263
reaction of colouring principles of,

- red ground, black and white on, 691

- mordant for, 287 - rose, 248

- salmon with, 94

- SCHLUMBERGER'S process for estimating utilisable tinctorial value of, 269

- style, catechu mixture for, 497

- styles, clearing, 313 - substitutes for, 329

- tinctorial matters of, 253 use and application of, 273varieties of, 236

- Zealand, 257

Madders, testing of, 269 Magenta, 93, 178, 184

- colouring linen yarn, 61

- printing, 185

Magenta, specimen, 186 Magentas, examination of, 185 - testing, 185 Magnesia in water, 11 Mahaleb, 512 Malates, 234 Malvaceæ, colouring matters of, 390 Manchester yellow, 222 Manganate of potash, 112 Manganese settlers, chloride of, 133 Mangrove, 512 Manilla, 107 Maroon, 94, 626 Marina, 232 Matters, amylaceous, 66 Mauvaniline, 182 Mauveine, 187 Measures of capacity, 700 Meekrapp, 228 Melin, 410 Mercerising, 281 Mercury, biniodide of, 152 — sulphide of, 152 Merino shade, bleaching cotton stockings, 51 - wool, 84 Methyl diphenylamine, 675

Mineral fibres, 16 - pigments, 148 — thickenings, 17 Mordant, black, 536 - for purples, 291 - HELLOT'S, 528 - new iron, 689 Mordants, 145, 275 - alkaline iron, 541

- alumina, 534 - aniline, 185 - antimony, 542 - arsenic, 545 - binary, 305 - bismuth, 543 - chromium, 544

copper, 545fixing of, by ageing, 280

- for brown, 292 - iron, 535 - lead, 541

manganese, 545methods of thickening, 286 - prescriptions of thickened, 287

- printing and fixing, 275

- tin, 519 - tungsten, 542 - zinc, 545

Morin, 407 Morinda citrifolia, root of, 391

Morindin, 391 Morintannic acid, 406 Mosaics, red for, 225 Mucilage, 233

Mucilage, various, 71 Mulberry tree, 104 Mummy-cloth, 21 Mungeet, 329 Murex brandaris, 171 Murexide, 168, 170, 219 discovery of, 168 Muriate of tin, 59, 523 Musa textilis, 64 Muslins, bleaching, 50 Myrobalans, 500

NAPHTHOLS, 680

Naphtha, brown, 208 Naphthalin colours, 220 - yellow, detection of, 672 Naphthylamin violet, 221 Neb-neb, 509 Negra, 351 Nitrate of ammonia, 121 - of iron, 61 — of potash, 111 — of tin, 60, 527 Nitro-benzol, 173 - detection of, 175 Nitro-coccussic acid, 357 Nitro-cuminic acid, 512 Nona, 329 Normal sulphuric acid, 122 Nucin, 512 Nuts, areca, 509 - Valonia, 500 Nut-galls, China, 500 Nymphæa alba, 512

CFNOLIN, 392

Oil employed in Turkey-red dyeing, 146

— Gallipoli, 321 Olive, bichrome, 96

cheap, 96zephyr, 97

Orange, 94, 633, 628, 636

- aniline, 209, 210 - with annatto, colouring linen yarn,

- anthracen, 681 - aurin, 217

- Blackley, 692

- with madder, colouring linen yarn, 60

Orcein, 375

Orchil, applications of in dyeing and printing, 379

- artificial, 694

paring, 376

- colouring matters of, 374

- liquor, to prepare, 377

- new methods of preparing, 375 - paste, ordinary method of preOrcin, preparation of, 374 pure, 373 Organic matter in water, 13 Orpiment, 154 Ouongkondou, 330 Oxalate of potash, 111 Oxide, chromic, 544

hydrochlorate of stannic, 530 Oxidiser, 133 Ozone, 74, 132

PADDING, 581

Para-carthamin, 512
Parelline or parellic acid, 374 Paste, cochineal, 88 - violet, test of, 191 Pastel, 453 Peachwood liquor, 60 Pectic acid, 40 Pectose, 234 Penseé brown, colouring linen yarn, 61 Peonine, 196 Perchloride, solution of, 536 Pericarpium, 64 Permanganate of potash, 112 — of soda, 119 Perrotine, working of, 554 Persian berries, 403 - detection of, 672 Phalæna mori, 104 Phenicienne, 207, 220, 674 Phenol, 215
— coloured derivatives of, 215 Phenyl, hydrate of, 215 Phenylation, 194, 197 Phormium tenax, 64, 107 Phosphate of soda, 119 Phosphine, 209 Phycocyan, 512 Phycoerythrin, 512 Phycohæmatin, 512 Phyllocymin, 435 Phylloxanthin, 435 Phytomelin, 410 Picramic acid, 219
Picric acid, aniline green with, 96 - - preparation of, 673 Picro-erythrine, 371 Pigment printing, 639
Pigments, blue and violet, 158 - green mineral, 156

— mineral, 148 — principal vehicles used for, 639

- red mineral, 152

Pine-apple plant, 64

- for listings, 93

Pincoffin, 262

- yellow mineral, 154

Pink, 225, 628, 633, 637, 638

- cochineal, specimen, 609

Pinks, for blocking madder work, 637 — plate, 575 Pistacia lentiscus, 500 Pittacal, 512 Plants, indigotin-producing, 448 Plaster of Paris, 150 Polish grain, 356 Polygonum tinctorium, 512, 454 Ponceau, 93, 187 - specimen, 186 - for woollen yarn, 629 Potash, 110, 126 - aluminate of, 278, 534 - bisulphate of, 111 - carbonate of, 127 -- caustic, 128 - chlorate of, 113 - chromate of, 111, 142 -- crude, 127 - hypochlorite of, 113, 139 - manganate of, 112 - nitrate of, III - oxalate of, 111 - permanganate of, 112 -- sulphindigotate, 445 - water-glass, 112 - in water, II - vat, 90 Pourpre Française, 378 Printing, 551 - ink, use of in calico printing, 688 — pigment, 639 Processes, discharge and resist. 317 Products, epidermic, 82 Prussian blue, colouring linen yarn, 61 Pseudopurpurin, 249, 252 Pterocarpus santalinus, 339 Purple, 225, 633, 637 — antline, 99 — colouring linen yarn, 61 - Byzantium, 171 -- heart, 512 - of the ancients, 171 - regina, 191 - SPILLER'S, 677 - - specimen, 677 - thickening for, 226 - Tyrian, 2, 171 Purples, murexide, 550 Purpurin, 242, 247, 252

— characters of, 249 — preparing, 248 — Dr. Schunck's researches on, 251 - to prepare a steam colour with, 309 Purpura, 171 Purpurates, 168 Purpuric acid, 168 Purpuroxanthin, 250, 252 Purrhee, 425 Purpura hemastoma, 171

Pink saffranine, specimen, 203

Pyrocatechin, derivatives of, 684

Quercitron, 395

- colouring matters contained in, 396

- decoction of, 395

- extract, detection of, 677

- use made of, 401

RAG dyeing, 653

Random, magenta, 103

- orange, 102 - purple, 103

- Prussian blue, 103 - Saxon blue, 102

- scarlet, 102

Randoms or clouded yarns, 102

Red, 225, 633, 638 - amaranth, 380

- brown, chrome, 97

- colouring linen yarn, 59

--- matters, 350 - harmala, 364

- HOFMANN'S xylidin, 675

- lakes, 365 - liquor, 277, 288

— madder, 93 — naphthylamine, 206

- new aniline, 689 - picric, 219

- and pink, madder, specimen, 576

- pink, mordants for, 275

prussiate, 163Turkey, with discharges, 565

- without oil, 225 - woods, chemical history of, 333

Reds, aniline, 178 - Coupier's aniline, 675 - detection of, 665

- thickening for, 226

Redoul, 501 Renegrida, 351

Resorcin, derivatives of, 684 - nitrous derivatives of, 685

Réserve, 318

Reserves, 319, 580, 585
— means of obtaining, 318

Resin, lac, 353 Resist, 318, 571 Rhamnoxanthin, 411

Rhea tenacissima, 63

Robbia, 228 Robium, 410 Roccellinine, 374

Rocon, 426 Rod, golden, 511

Roller printing, steam black for, 347

Root, Carapa, 510 - yellow Canadian, 510

Rosanaphthylamine, 206

Rosaniline, acetate of, 183

- hydrochlorate of, 181

- preparation of, 179 Rose colour, mordants for, 275

— pink, 93 — — mordants for, 288

Roseine, 178 Rosolic acid, 674, 683

Rothine, 220 Rubia, 228

- cordifolia, 229

- mungista, 329

- peregrina, 229

- tinctorium, 228

Rubiaceæ, products of, 328

Rubiacin, 251

- (SCHUNCK), 252

Ruberythric acid (Rochleder), 252

Rutin, 410 Rutinic or rutic acid, 410 Rufi gallic acid, 687

SAFFLOWER, 384

- estimation of goodness of, 386

- varieties of, 385 Saffranin, test for, 689

Saff. anin, 207 Saffron, 422

Sal-ammoniac,121 Salmon, 94

- with madder, 94

Santalin, 340 Salt, preparing, 532 - pink, 532

Salts, ammoniacal, 120

Saw-wort, 513

Scales, thermometer, 699 Scarlet, 92, 635

- cochineal, 92

- for delaines, 623 - grain, 353

— lac-dye, 92 — Ulrich's, 676

- for woollen yarn, 630

SCHUNCK, Dr., constituents of cotton fibre, 29

Shades, covering, 581—heavy, prepare for, 600

Shellac, 354 Shumach, 501 Silica, 110

ultramarine, 161 Silicate of soda, 118

Silk, 104

- bleaching, 106

- constitution of, 104
- black, detection of, 672
- and other fibres, means of distinguishing, 107 Silks, method of dyeing, 630

Terra Japonica, 490 Silkworm, 104 Singeing, 654 Sizal, 107 Slate, 99 - colouring linen yarn, 62 - purple, 99 Slates and modes on white warps, 100 Soap, 312 - baths, 312 Soaping, 309 Soda, aluminate of, 279, 534 - ash, 113, 127 — Barilla, 113 - carbonate of, 113 - carminate of, 357 - caustic, 129 - hypochlorite of, 119, 139 - hyposulphite of, 119 - permanganate of, 119 - phosphate of, 119 - plumbate of, 541 - salts, 113 - silicate of, 118 - stannate of, 532 - stannite of, 526, 681 - sulphate of, 113 - tungstate of, 119, 542 - ultramarine, 161 - valuation of, 118 - vat, 90 — waste, 115 — utilisation of, 117 - in water, 11 — water-glass, 118 Sodium, chloride of, 119 - hydroxide of, 129 Solution, litmus, 122 Solutions, test, 122 Sooranjee, 391 Sorgho, colouring matters contained in, 389 Souring, 48 Spirit, amaranth, 524 aniline, 528 - barwood, 531 - claret, 526 - another finishing scarlet, 525 - methylated, 200 - plum, 531 - purple cotton, 532 — plum, or puce, 525 — for wool, 528 - scarlet finishing, 525 - another yellow, 525 - yellow and orange, 525 Spirits, bowl, 527 - crimson, 530

- protartar, 549

- of salts, 520

red cotton, 530royal blue, 550

Spirits, scarlet, 521, 527 Substances, albumenoid, 73 - soluble in boiling water, 234 Substitutes for albumen, 81 Stannic oxide, 519 Starch, 66 Steam chest, 599 - style, 598 Stick-lac, 353 - varieties of, 354
Stockings, bleaching cotton, with Turkey-red tops, 52 - cotton, merino shade bleachings, 51 Stone, blue, 547 - colour, 99 - - steam, 611 Style, indigo, first stage, specimen, 590 - - second stage, specimen, 591 -- with other colours, specimen, 591 - lazulite, 587 - madder, first stage, specimen, 577 - after dyeing, specimen, 577 - - after clearing, specimen, 578 - neutral, 587 plate, 575produced by Lightfoot's patent process, specimen, 592 - reserved, 564, 580 - (sixth), China blues, 593 - (eighth), 598 Styles, madder, 567 — padding, 565 — pigment and other, 641 Sulphate of baryta, 151 --- ferric, 536 — ferrous, 535 — of lime, 150 - of soda, 113 Sulphindigotic acid, 445 Sulphur, recovery of, 117 Sulphurique, charbon, 247 Suint, 85 Sumac, 501
— chief varieties of, 501 Sumach, 501 Sunflower seeds, 513 Superargol, 550 " Syria," 513 TABLES, hydrometer, 696

Tannin, 189, 502

— estimation of in nut-galls, 503

Tartar, 112, 548

— cake, 550

— emetic, solution of, 502

— essence of, 549

— liquid, preparation of, 549

— substitutes for, 549

Tartrates, alkaline, 234

Terminalia Chebula, 500

Terra Japonica, 490 Thibets, silk-striped, black for, 100 Thickeners, 563 Thickenings, mineral, 17 - vegetable, 17 Tном, Mr., singeing cotton fabric, 44 Thuya occidentalis, colouring matter of, 411 Tin, bichloride of, 530 - binoxide of, 519

- bisulphide of, 154 crystals, 59double muriate of, 523

- mordants of, 519 - muriate of, 59 - nitrate of, 60, 527 - nitro-muriate of, 528

- oxalate of, 525 - oxymuriate of, 532 - perchloride of, 530 - peroxide of, 519 - per-salts of, 529

- protochloride of, 522 - proto-salts of, 522 - salt bath, 313 - sesqui-salts of, 526 - sesquioxide of, 519

- single muriate of, 524 - solution of, 523, 531 - solutions of proto-salts of, 524

- spirits, 519 - stannic, chloride of, 530 - sulpho-muriate of, 630 - tetrachloride of, 330

- pulp, blue, 166 - white, 166 Toluen, 222, 675 Toluidine, 177

- discovery of, 177 Trimethylic rosaline, bimethyl iodhydrate of, 202 Tungstate of soda, 119

Turkey red, 321

- — experiments on, by Dr. Schüт-ZENBERGER, 323

- - tops, bleaching cotton stockings with, 52

- reds, discharges on, 594 Turmeric, 418

Turning, 654 Tyrian purple, 2

TTLTRAMARINE, 158

- and madder extract, specimen, 643 - blue, chrome black, and dichromate of lead, specimen, 641

- manufacture of, 159

- materials for manufacture of artificial, 160

- silica, 161

Ultramarine, soda, 161 — specimen of, 160 Urtica utilis, 63 Usitatissimum linum, 57

7AT blues, detection of, 672

- decomposed, 90

- Indian or potash, 480 - soda or potash, 90

Vats, indigo, 471

— pastel, 479 Variolaria dealbata, 369

Vegetable and animal origin, colouring matters of, 228

- fibres, 17

- distinguishing from each other,

— thickenings, 17, бб Verdigris green, 545 Vermillion red, specimen, 153

Vesuvine, 220

Violaniline, 183, 209 Violet, amaranth, 380 - Ballo's, 679

- Dorothea, 676 - HOFMANN'S, 192, 613, 676 - - specimen, 194, 677

- imperial, 190 — Lauth's, 677

- methyl diphenylamine, 678 - Paris, 676

or mauve, Perkin's, 187
Poirrier's, 676

- WANKLYN, 676 Violets, detection of, 667 - naphthylen diamine, 221 - naphthylamine, 221 Viscosimeter, STEILMANN's, 71

Vitriol, blue, 547 green, 535 - Roman, 547

W^{ASHING-MACHINE, 308}

Water, phenylated, 215—test for impurities, 10 Water-glass, potash, 112 - soda, 118 Wau (German), 408 War cotton, 30, 34 Weld, 408 - cultivation of, 408

- dyeing with, 413 - - upon cotton, 414

- mode of extracting colouring matter from plant, 409

Weights, 701 - and measures, decimal or metric, 699 Whinberries, 509 White, 639

White colouring matters, 150 - warps, green on, 101

- slates and modes on, 100 Whortleberries, 509

Wine, hermitage, 259

— red colouring matters of, 392 Woad, 89, 453

- vat, applications of, 90

Wolfram, 542 Wongsky, 421

Wood, Bahamas or Jamaica, 332

— Bahia, 332 — Brazil, 331

-- colouring glucoside, 335 - - decoction or liquor of, 337

- caliatur or cariatur, 341

- Californian, 332 - cam or kambe, 342

- Cuba, 105

- Madagascar, 341 - Nicaragua, 332

- palisander, 512 - Pernambuco, 331

- santal, 340

- - sanders, or red sanders, 339

- sapon or sappan, 332 - Sierra Firma, 332 - St. Martha, 331

- yellow, 405 Brazil, 405 Woods, red, 331 Wool, 82, 652, 674

- bleaching, 86 - merino, 84

- reds on, 92 - sulphur from, 85 Woollen fibre, 83

Woollen yarn and fabrics, recipes in connection with, 88 - bleaching, 88 Woollens, colours on, 89

Working, 654 Wouw (Dutch), 408

XANTHEIN, 424

Xanthin, 424 Xanthopurpurin, 249, 252 Xanthorrhea hastilis, 218

VARN, green for, 95

white bleaching linen, 58 Yellow, 94, 628, 635, 638

- Belge, 94

- campo-bello, 674 - colouring linen yarn, 59

- coralline, 217 -- dark, from Persian berries, speci-

men, 612 - Fol's, 674

- French, 678 - Indian, 425

- naphthalin, 221 - pale, from Persian berries, speci-

men, 612 Yellows, aniline, 209 - detection of, 664 Yokin, 418

ZINALINE, 210

Zinc, anhydrous oxide of, 151 - chloride of, 523, 545

ERRATA AND ADDENDA.

P. 93, line 3 from bottom, for "saleratus" read "bicarbonate of soda."

P. 226, line 8, for "lime" read "iron."

P. 239. The formula of alizarin is now considered to be C₁₄H₈O₄.

P. 438, line 14 from bottom, read "a perfectly definite nitrogenous principle."
,, line 6 from bottom, for "chemistry" read "compounds."

P. 439, line 22 from bottom, erase " and chlorine."

P. 440, line 6 from bottom, for "sulphuric acid" read "sulphurous acid."

P. 447, line 24, for "found" read "formed."

", line 10 from bottom read "in certain animal secretions, such as urine, not merely pathologically, but as a result of ordinary metamorphosis of tissue (see Schunck on the Occurrence of Indigo Blue in Urine)."

P. 468, line 7 from bottom read "enluminage."

P. 470, line 19 from bottom read "that trials in practice on the large scale differ from."

P. 472, line 15 from bottom, for "active" read "process."

P. 476, note, erase "by porosity through the fibre."

P. 534, line 3, after "cotton-yarn" insert "it."

P. 539, line 17, for "nitric acid" read "nitrate of iron."

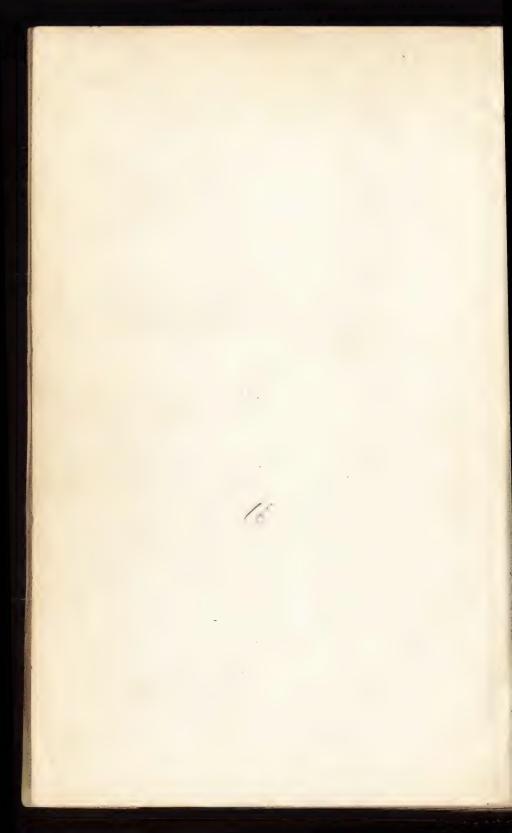
P. 553, line 10 from bottom, erase "throws."

P. 651, line 20, for "chiefly" read "sometimes."

,, line 26, for "woven" read "unwoven."

P. 654, line 6 from bottom:—In an improved machine there are two rollers fixed over the beck. The goods run over one roller, through the liquor, and on the other roller. By reversing the handle the pieces are alternately coiled and uncoiled round each roller.

P. 665 (Detection of Reds):—To distinguish saffranin from magenta boil the swatch in alcohol. If it is magenta the solution will appear crimson and transparent, both by reflected and by transmitted light; whilst saffranin solution is rose-colour and transparent by transmitted light, but appears turbid, opaque, and scarlet by reflected light. Warm water containing 5 per cent of soap becomes coloured if a swatch dyed with magenta is steeped in it, but remains colourless if the dye be saffranin. If a swatch is steeped in water acidulated with hydrochloric acid, along with a piece of zinc, it will soon be decolourised if the dye is magenta; saffranin remains unchanged for some time, and then turns a bright yellow.





HXN.LX 13252

47 52 0 /9

SPECIAL 9479 TP 930 C94 1874

> THE GETTY CENTER LIBRARY



CROOKES DEYING & CALICO-PRINTING